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A Mechanism of Acquirement of Cosmic-Ray Energies by Electrons

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(Received December 27, 1932)

It is shown that the growth of stellar magnetic fields such as occur in sunspots can give rise according to Faraday's law of electromagnetic induction to electric fields capable of giving electrons energies corresponding to 10^{10} volts. Moreover, the rate of acquirement of energy can reasonably be greater than the rate of loss by collisions with atoms. It would be difficult to realize energies as high as 10^{10} volts from the magnetic fields of spots such as occur on the sun. Energies corresponding to 10^{9} volts are, however, within the range of possibility, and it is suggested that electrons projected from such spots may play a part in auroral phenomena. For cosmic rays one must, however, probably look to the stars for the necessary conditions. Because of the repulsion of the current responsible for the magnetic field, the electron is hurled away from the spot as it acquires its energy.

IT is usually considered that the assumption of the existence of electronic energies of the order 10^{10} volts is attended with considerable theoretical difficulties. The present note is an elaboration of one of the suggestions recently made by the writer.[1] It concerns the possibility of the production of cosmic-ray energies in stellar spots, analogous to sunspots on our sun. It is known that the sunspots possess considerable magnetic fields which grow in comparatively short intervals of time. A consideration of the existing magnitudes will show that line integrals of the electric field of the order 10^{10} volts may readily arise through the Faraday law as a result of the growth of such magnetic fields. However, the detailed working out of the matter involves certain considerations which require careful attention.

We shall consider the problem in cylindrical polar coordinates r, θ, z, in which the stellar spot is in the plane of r, θ, and the magnetic field H is symmetrical with θ and, of course, more or less perpendicular to the plane of the spot.

The problem must be treated from the standpoint of relativistic electrodynamics. It may be conveniently treated by the equations of Lagrange, or even more conveniently by the Hamiltonian equations.

The Lagrangian function for an electron in a field specified by a vector potential U and a scalar potential φ is, as is well known

$$L=-mc^2(1-\beta^2)^{\frac{1}{2}}+(e/c)(\mathbf{U}\cdot\mathbf{u})-e\varphi,$$

where m is the rest mass, u is the velocity, and $\beta^2=u^2/c^2$.

φ is zero in our problem, so that transforming to polar coordinates, we have

$$L=-mc^2\left(1-\frac{r^2\dot{\theta}^2}{c^2}-\frac{\dot{r}^2}{c^2}-\frac{\dot{z}^2}{c^2}\right)^{\frac{1}{2}}+\frac{e}{c}(\dot{r}U_r+r\dot{\theta}U_\theta+\dot{z}U_z).$$

[1] In a paper under the above title presented at the Chicago Meeting of the American Physical Society, November, 1932.

The momenta P_r, P_θ, P_z, are given by

$$P_r = m\dot{r}(1-\beta^2)^{-\frac{1}{2}} + eU_r/c, \tag{1}$$

$$P_\theta = mr^2\dot{\theta}(1-\beta^2)^{-\frac{1}{2}} + erU_\theta/c, \tag{2}$$

$$P_z = m\dot{z}(1-\beta^2)^{-\frac{1}{2}} + eU_z/c. \tag{3}$$

The Hamiltonan function $\mathfrak{H}$ is given by

$$\mathfrak{H} = \dot{r}P_r + \dot{\theta}P_\theta + \dot{z}P_z - L \tag{4}$$

and is easily shown to be $\mathfrak{H} = mc^2(1-\beta^2)^{-\frac{1}{2}}$. Solving (1), (2) and (3) for $\dot{r}$, $\dot{\theta}$, $\dot{z}$, and substituting in (4) we readily find

$$\mathfrak{H} = mc^2\left\{1+\frac{1}{m^2c^2}\left[\left(P_r - \frac{e}{c}U_r\right)^2 + \left(\frac{P_\theta}{r} - \frac{e}{c}U_\theta\right)^2 + \left(P_z - \frac{e}{c}U_z\right)^2\right]\right\}^{\frac{1}{2}}. \tag{5}$$

Now in our problem $U_r = U_z = 0$, and U_θ is independent of θ for a magnetic field symmetrical with regard to θ. In fact, the electron currents responsible for U are all of a circular type symmetrical about the z-axis. Thus P_θ is constant, i.e., from (2)

$$mr^2\dot{\theta}(1-\beta^2)^{-\frac{1}{2}} + erU_\theta/c = er_0U_0/c, \tag{6}$$

where r_0 and U_0 refer to the values of r and U_θ at the initial instant when $\dot{\theta} = 0$. Thus

$$\mathfrak{H} = mc^2\left\{1+\frac{1}{m^2c^2}\left[P_r^2 + P_z^2 + \frac{e}{c}\left(\frac{r_0U_0}{r} - U_\theta\right)^2\right]\right\}^{\frac{1}{2}}. \tag{7}$$

Now $\mathfrak{H}$ is explicitly a function of t through U_θ. Hence, as follows directly from the Hamiltonian equations

$$d\mathfrak{H}/dt = \partial\mathfrak{H}/\partial t = -(e^2/\mathfrak{H})(r_0U_0/r - U_\theta)(\partial U_\theta/\partial t)$$

$$\tfrac{1}{2}d\mathfrak{H}^2/dt = e^2(U_\theta - r_0U_0/r)(\partial U_\theta/\partial t). \tag{8}$$

Since $\mathfrak{H} = mc^2(1-\beta^2)^{-\frac{1}{2}} = T + mc^2$, where T is the kinetic energy,

$$\tfrac{1}{2}(d/dt)(T+mc^2)^2 = e^2(U_\theta - r_0U_0/r)(\partial U_\theta/\partial t). \tag{9}$$

Hence T increases with t so long as $rU_\theta \geq r_0U_0$. This is certainly satisfied at the initial instant in view of the definitions of r_0 and U_0. It will be satisfied for all subsequent instants if $d(rU_\theta)/dt \geq 0$; i.e., if $\partial U_\theta/\partial t + (\dot{r}/r)(\partial/\partial r)(rU_\theta) \geq 0$; i.e., if

$$-(E_\theta - \dot{r}H_z/c) \geq 0. \tag{10}$$

Bearing in mind that E_θ is in the negative direction of θ for an increase of U_θ in the positive direction of θ, we see that condition (10) is simply the condition that the force due to the electric field accelerating the electron in the negative direction of θ must be always greater than the force due to the magnetic field which acts in the opposite sense when $\dot{r}$ is positive. If (10) is satisfied always, the electron will never loop around in its path since to so loop $-(E_\theta - \dot{r}H_z/c)$ would have to be less than zero in order to balance the centrifugal acceleration at the instant when $\dot{\theta}$ was zero. Since $\dot{r}$ can never exceed c, the condition for continual increase of energy will always be satisfied if $|E| > |H_z|$. If there is anything like a uniform growth of magnetic flux with time, E will certainly be greater than H initially, and we shall find that there is time for high electronic energy to be acquired before H has grown to a magnitude sufficiently large to prohibit further increase.

If the electron starts from rest, at $t = 0$ and if the magnetic field is zero then we have $U_0 = 0$, and

$$\tfrac{1}{2}(d/dt)(T+mc^2)^2 = e^2U_\theta(\partial U_\theta/\partial t). \tag{11}$$

So far we have made no assumption as to the way in which the magnetic field H depends upon r. Since $H = \text{curl } U$, Stokes theorem applied to an annulus $2\pi r dr$ perpendicular to z gives

$$2\pi rH_z = \partial(2\pi rU_\theta)/\partial r. \tag{12}$$

If, for purposes of illustration we take a case where H_z is inversely proportional to r, we shall enjoy the advantage of having U_θ independent of r as well as of θ. We shall consequently write

$$H_z = H_0Rt/r\tau \tag{13}$$

where τ is the time taken for it to acquire a field intensity H_0 at some assigned radius R comparable with the radius of the spot.

With U_θ independent of r and $U_r = 0$, $\mathfrak{H}$ is independent of r, so that P_r is constant with time, which, through (1) shows that $\dot{r}$ is zero for all time since it is zero initially. Thus the electron describes a circular path. As a matter of fact

an examination of the equations shows, as might be expected, that, under these conditions, the centrifugal acceleration of the electron and the magnetic deflecting force increase together with the time in such a manner as to keep each other balanced.

Thus, with the assumption involved in (13), (12) gives $U_\theta = H_0 R t/\tau$ and (11) gives

$$(d/dt)(T+mc^2)^2 = 2e^2H_0^2R^2t/\tau^2 \qquad (14)$$

and $(T+mc^2)^2 = e^2H_0^2R^2t^2/\tau^2 + m^2c^4$. Since T is zero when t is zero.

For the energies in which we are interested, energies of the order 10^{10} volts, mc^2 is negligible, so that $T = eH_0Rt/\tau$ or, expressed in volts, $V = 300H_0Rt/\tau$. If $R = 3\times10^{10}$, $H_0 = 2000$, $\tau = 10^6$, $t = 1$ second, we find $V = 2\times10^{10}$ volts.

The conclusion is then to the effect that in one second during the initial formation of a stellar spot about 50 times the earth's diameter and of such character as to give rise to a magnetic field of 2000 gauss in 12 days, an electron can acquire a velocity comparable with 2×10^{10} volts. The electric field E is given by

$$\int_0^R \frac{H_0 R}{r\tau} 2\pi r dr = 2\pi RcE,$$

so that $E = H_0R/c\tau$ and the magnetic field at the end of a time t is H_0t/τ. Hence in the present instance, the magnetic field would only just have attained a value equal to the electric field by the time the electron had received 2×10^{10} volts velocity. In the present case, the fact that $\dot{r}$ is zero insures that the electron would go on acquiring energy continually, even after the magnetic field had become equal to or greater than the electric field; but, this feature is special to our particular assumption as to the dependence of the magnetic field upon r. Naturally our particular assumption regarding H is mainly relevant only to the mathematical simplification of the problem and not to its essential features. As a matter of fact the magnetic field we have assumed would not have zero curl, and would require the existence of circular electron currents in the regions where H has the property specified. Difficulties regarding the infinite value of H at $r = 0$ are irrelevant since we only require the variation of H with r postulated to exist over a very thin range of r. If we had a uniform magnetic field instead of one of the type assumed, the electron would not describe a circular orbit but would diminish its distance from the origin in its path. This complicates the details of our calculation but not the order of magnitude of the results.

We have given no attention to the motion of the electron parallel to z. It is obvious that since the electronic motion takes place in the opposite sense to that of the increasing electronic currents which are producing the magnetic field, the electron will be repelled from them, and so will shoot out into space, which is a desirable consummation from the point of view of our theory.

An examination of the foregoing calculation shows that it would be difficult to secure energies of 10^{10} volts from spots of a size such as occur on our sun. However, energies one-tenth of this amount are within the range of possibility. This fact is particularly interesting in suggesting that while we may have to look to stars other than our sun for sources of cosmic rays, the spots on the sun may be able to furnish electrons such as could play a part in auroral phenomena, since the position of the auroral zone suggests energies of the order of 10^9 volts for the electrons producing auroras. It is moreover a significant fact in this connection that correlations between sunspot activity and auroral and terrestrial magnetic phenomena have been observed. Another matter of significance arises from the fact that although, for purposes of visualization of the situation, we have imagined a spot which grows 2000 gauss in 10^6 seconds, as a matter of fact the electronic energy of 2×10^{10} is acquired before the spot has been growing for more than one second, or before the field has attained a value of more than 2×10^{-3} gauss in our example. Naturally it is not intended to imply that a situation exists in nature in which the problem we have cited is duplicated in all its details. All that it is intended to show is that with magnetic fields extending over large areas in stellar spots, relatively small rates of changes of these fields existing for brief periods can give rise to large electronic energies. Our problem has been designed to illustrate the feasibility of the idea in one particular case.

Finally, we must consider the possibility of

loss of energy by collision. The work done on the electron over its mean free path λ is $E\lambda e$. In our present example $E = RH_0/\tau c = 2\times 10^{-3}$ e.s.u. Hence the work estimated in volts is $10^{-3}\times 600\lambda = 0.6\lambda$ volt. Hence if λ were greater than 50 cm the electron would acquire more energy over its mean free path than it would lose at collision, and the energy would continue to increase with time. The pressure above the surface of a star falls off very rapidly with distance and is probably far below that corresponding to a mean free path of 50 cm in regions which are sufficienty near to the surface to experience the magnetic fields of the spots. It is probable, therefore, that the efficiency of the process of accumulation of energy is but little reduced by collisions.

Interpretation of X-Ray Satellites

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(Received January 5, 1933)

Druyvestyn's explanation of the $K\alpha$ satellites has been put to the test of numerical calculation using the Hartree field in the case of potassium ($Z=19$). The $K\alpha$ satellites are attributed to transitions from states with one K and one L electron missing to states with two L electrons missing. Treating e^2/r_{12} as a perturbation and using the wave functions of the unperturbed Hartree wave equation, the energies belonging to the configurations $1s\,2s$, $1s\,2p$, $2s\,2p$, and $(2p)^2$ were calculated according to Slater's theory of complex spectra. The symbols describing the configurations refer to electrons missing from closed shells. The assumption of Russell-Saunders coupling is a justifiable approximation since the interchange energies turn out to be large compared with the spin-orbit interaction, which is measured by the $K\alpha_{1,2}$ doublet separation. There are five allowed transitions which may be correlated with five characteristic $K\alpha$ satellites. $K\alpha_{5,6}$ are not observed in potassium but appear in other elements as a doublet at higher frequency than $K\alpha_{3,4}$. A small change in the interchange integrals would reverse the sequence of the frequencies calculated for $K\alpha_3$ and $K\alpha_4$ and likewise for $K\alpha_5$ and $K\alpha_6$. The reason for choosing the transitions assigned here is to make $K\alpha_3$ and $K\alpha_5$ appear as triplet-triplet transitions, since these lines have fine structure. The strong lines, $K\alpha_{3,4}$, which persist from $Z=11$ to $Z=30$, are due to an initial $KL(2_1)$ ionization. The weak lines, $K\alpha'$ and $K\alpha_{5,6}$, which appear from $Z=11$ only to $Z=19$ and $Z=16$, are due to an initial $KL(2_2)$ ionization.

Line	ν/R obs.	Transition	ν/R calc.
$K\alpha'$	245.05	$1s\,2p\ {}^1P\rightarrow(2p)^2\ {}^1S$	245.05
$K\alpha_3$	245.56	$1s\,2s\ {}^3S\rightarrow 2s\,2p\ {}^3P$	245.63
$K\alpha_4$	245.69	$1s\,2s\ {}^1S\rightarrow 2s\,2p\ {}^1P$	245.53
$K\alpha_5$	—	$1s\,2p\ {}^3P\rightarrow(2p)^2\ {}^3P$	246.38
$K\alpha_6$	—	$1s\,2p\ {}^1P\rightarrow(2p)^2\ {}^1D$	246.15

THE object of this paper was to put to the test of numerical evaluation in a special case the predictions of some of the theories of the origin of x-ray satellite lines.

On the hard side of the $K\alpha$ lines, satellites are observed over the atomic number range 11 to 30. Six satellites are observed, though not all are found for any one element, and are called $K\alpha''$, $K\alpha'$, $K\alpha_3$, $K\alpha_4$, $K\alpha_5$, $K\alpha_6$, in order of increasing frequency. It was early suggested by Wentzel[1] that these lines might result from single electron transitions in atoms doubly ionized in the x-ray levels—thus analogous to spark lines in optical spectra. Experiments on excitation potential have shown that the details of Wentzel's scheme were wrong, since it called for double ionization in the K shell as the initial state for some of the satellites.

The experimental technique of measuring ionization potentials is so difficult that it has not been possible to prove whether energy enough for ionization in the K shell and in the L shell is necessary for the appearance of the $K\alpha$ satellites. Dumond and Hoyt[2] believe that the excitation potential of $K\alpha_{3,4}$ in Cu ($Z=29$) is probably less than the sum of the K and L ionization energies, but this conclusion is based on an extrapolation and is not conclusive.

Druyvestyn[3] has revised the theory of Wentzel. He assigns the following transitions to the $K\alpha$ satellites, where the symbol K means one electron missing from the K shell, etc. (see Table I). We shall use hereafter the spectroscopic notation, $1s$ instead of K, etc. In support of these assignments, Druyvestyn has given a rather naive treatment of the theory of single and double ionization by electron impact according to which the relative intensities of the satellites and their falling off in intensity relative to the diagram

TABLE I.

$K\alpha'$	$KL(2_1)$	$\rightarrow L(2_2)L(2_1)$	$1s\,2s\ \rightarrow 2p\,2s$
$K\alpha_{3,4}$	$KL(2_2)$	$\rightarrow L(2_2)L(2_2)$ or	$1s\,2p\ \rightarrow(2p)^2$
$K\alpha_{5,6}$	$KL(2_2)L(2_2)$	$\rightarrow L(2_2)L(2_2)L(2_2)$	$1s\,(2p)^2\rightarrow(2p)^3$

[1] Wentzel, Ann. d. Physik **66**, 437 (1921).

[2] Dumond and Hoyt, Phys. Rev. **36**, 799 (1930).

[3] Druyvestyn, *Dissertation*, Groningen, 1928; Zeits. f. Physik **43**, 767 (1927).

line with increasing atomic number come out more or less right. The frequencies have not previously been calculated.

Langer[4] has suggested that complex spectra are to be expected when two or more electrons are missing in inner shells and has pointed out that the transitions $1s\ 2s \rightarrow 2p\ 2s$, $1s\ 2p \rightarrow (2p)^2$ give rise to five lines and might account for the satellites.

We undertook to calculate the frequencies of these five lines for the case of potassium, $Z=19$. Heisenberg[5] has shown that Slater's theory of complex spectra[6] applies just as well to electrons missing from closed shells as to electrons present outside closed shells. Accordingly, we proceeded to calculate the energy levels of the configurations $1s\ 2s$, $1s\ 2p$, $2s\ 2p$, and $(2p)^2$ according to Slater's theory. The levels predicted are (Slater,[6] page 1315 and page 1316) given in Table II.

TABLE II.

$1s\ 2s$	$\begin{cases} {}^1S = J(100, 200) + K(100, 200) = F^0(10, 20) + G^0(10, 20) \\ {}^3S = J(100, 200) - K(100, 200) = F^0(10, 20) - G^0(10, 20) \end{cases}$
$1s\ 2p$	$\begin{cases} {}^1P = J(100, 211) + K(100, 211) = F^0(10, 21) + \frac{1}{3}G^1(10, 21) \\ {}^3P = J(100, 211) - K(100, 211) = F^0(10, 21) - \frac{1}{6}G^1(10, 21) \end{cases}$
$2s\ 2p$	$\begin{cases} {}^1P = J(200, 211) + K(200, 211) = F^0(20, 21) + \frac{1}{3}G^1(20, 21) \\ {}^3P = J(200, 211) - K(200, 211) = F^0(20, 21) - \frac{1}{6}G^1(20, 21) \end{cases}$
$(2p)^2$	$\begin{cases} {}^1S = F^0(21, 21) + 10/25F^2(21, 21) \\ {}^1D = F^0(21, 21) + 1/25F^2(21, 21) \\ {}^3P = F^0(21, 21) - 5/25F^2(21, 21) \end{cases}$

The expressions in terms of F and G are found by substituting the values of a^k and b^k from the tables (Slater,[6] page 1312) into the general expressions for $J(nlm, n'l'm')$ and $K(nlm, n'l'm')$ (Slater,[6] p. 1311). The integrals F^k and G^k are defined (Slater,[6] page 1311) as

$$F^k(nl, n'l') = e^2 \int_0^\infty \int_0^\infty R_{nl}^2(r) R_{n'l'}^2(r') r_a^k / r_b^{k+1} r^2 r'^2 dr\, dr'$$

$$G^k(nl, n'l') = e^2 \int_0^\infty \int_0^\infty R_{nl}(r) R_{n'l'}(r) R_{nl}(r') R_{n'l'}(r') r_a^k / r_b^{k+1} r^2 r'^2 dr\, dr'.$$

Here R_{nl} is the solution of the radial part of the unperturbed wave equation for one electron. By r_a is meant the smaller and by r_b the larger of the values r and r'. We have dropped a factor $4\pi^2$ since we normalize R_{nl} to unity rather than to $1/(2\pi)^{1/2}$ as Slater does.[7]

The work which is being reported here was the calculation of the various F^k and G^k integrals required to determine the energy levels of the four configurations in which we are interested. The method used was numerical integration and the wave functions used were those of the Hartree self-consistent field[8] for potassium. Having available the data on the self-consistent field of the potassium ion, i.e., potassium with the valence electron missing, we proceeded to solve the radial wave equation numerically, obtaining the wave functions R_{10}, R_{20}, R_{21}. The potential energy function in the wave equation in each case was that of the potassium ion less that of the particular electron whose wave function was to be found.

TABLE III.

$F^0(10, 20) = 6.38$	$G^0(10, 20) = 1.12$
$F^0(10, 21) = 7.50$	$G^1(10, 21) = 0.74$
$F^0(20, 21) = 4.76$	$G^1(20, 21) = 3.5$
$F^0(21, 21) = 5.44$	$F^2(21, 21) = 3.05.$

Using these wave functions, we calculated the following integrals in Table III. The numerical values given are in the customary ν/R units. The fact that the interchange integrals, the G's and F^2, turn out to be large compared to the spin-orbit interaction energy, which is measured by the doublet separation of $K\alpha_{1,2}$ and amounts to 0.23, shows that we are justified in neglecting the spin-orbit interaction and using as an approximation the Slater theory which assumes Russell-Saunders coupling.

The multiplet energies obtained by substituting the values from Table III in the formulas

[4] Langer, Cleveland Meeting, Phys. Rev. **37**, 457 (1931).

[5] Heisenberg, Ann. d. Physik **10**, 888 (1931).

[6] Slater, Phys. Rev. **34**, 1293 (1929).

[7] Condon and Shortley, Phys. Rev. **37**, 1026 (1931). Remark on normalization.

[8] Hartree, Camb. Phil. Soc. Proc. **24**, 89 (1927). Since the wave functions must have been worked out in the process of finding the self-consistent field, it would pay anyone who wished to do more work of this sort to obtain the complete solutions from Hartree for those atoms which have been studied by him. We had a table of the values of $Z(r)$ as a function of r, sent to us by Miss Phillips at Berkeley and originally obtained by her from Hartree.

of Table II are perturbation energies—the perturbation being the electrostatic interaction e^2/r_{12} between two electrons present outside closed shells or missing inside closed shells—to be measured from the unperturbed levels which are, for each configuration, the sum of the ionization energies of the two electrons separately. In each of the transitions which we shall consider, one electron is common to the initial and final configurations while the change in the ionization energy of the other corresponds to the energy of the $K\alpha_{1,2}$ doublet. Thus we must add 243.96, the ν/R value of the center of gravity of $K\alpha_{1,2}$, to the ν/R differences given by Table II to get the ν/R values predicted for the various allowed transitions.

In Table IV, we list the transitions that are allowed according to the spectroscopic rules in cases of Russell-Saunders coupling and the predicted ν/R values. We correlate these with the five $K\alpha$ satellites and list the ν/R values for those that are observed. The last column shows the transitions assigned by Langer to the various $K\alpha$ satellites. $K\alpha_{5,6}$ are not observed in potassium but appear in other elements as a doublet at higher frequency than $K\alpha_{3,4}$.

TABLE IV.

Line	ν/R obs.	Transition	ν/R calc.	Langer's assignment
$K\alpha'$	245.05	$1s\,2p^1P \rightarrow (2p)^2\,{}^1S$	245.05	$1s\,2s^1S \rightarrow 2s\,2p^1P$
$K\alpha_3$	245.56	$1s\,2s^3S \rightarrow 2s\,2p^3P$	245.63	$1s\,2p^3P \rightarrow (2p)^2\,{}^3P$
$K\alpha_4$	245.69	$1s\,2s^1S \rightarrow 2s\,2p^1P$	245.53	$1s\,2s^3S \rightarrow 2s\,2p^3P$
$K\alpha_5$	———	$1s\,2p^3P \rightarrow (2p)^2\,{}^3P$	246.38	$1s\,2p^1P \rightarrow (2p)^2\,{}^1S$
$K\alpha_6$	———	$1s\,2p^1P \rightarrow (2p)^2\,{}^1D$	246.15	$1s\,2p^1P \rightarrow (2p)^2\,{}^1D$

It will be noted that the frequency correlation would be better if we interchanged the transitions assigned to $K\alpha_3$ and $K\alpha_4$. Similarly, $K\alpha_6$ should have a higher frequency than $K\alpha_5$. But a small change in the interchange integrals, which were calculated much less accurately than the screening integrals, F^0, would bring these frequencies into the right sequence. The reason for choosing the assignments as we have done is to make $K\alpha_3$ and $K\alpha_5$ appear as triplet-triplet transitions. These lines are generally diffuse and fine structure has been observed in them for some elements.

It is observed that $K\alpha_{3,4}$ are much stronger than $K\alpha'$ and $K\alpha_{5,6}$. Also the range of atomic numbers for which $K\alpha_{3,4}$ are observed is 11 to 30, while for $K\alpha'$ it is 11 to 19 and for $K\alpha_{5,6}$ it is 11 to 16. This correlates nicely with our assignment of $K\alpha_{3,4}$ to one initial configuration, $1s\,2s$, and the other lines to the other initial configuration, $1s\,2p$. This suggests that a correct theory of double ionization *might* show a greater probability for the ionization $KL(2_1)$ than for the ionization $KL(2_2)$.

While the use of the Hartree atom is an approximation and we do not claim any high order of accuracy for our numerical work, it seems to us that the correlation between the observed and calculated behavior of the satellites is so striking as to make our interpretation seem very reasonable.

The satellite $K\alpha''$, which has been left entirely out of account here, lies much nearer to $K\alpha_{1,2}$ than the rest and is assigned by Druyvestyn to a transition $KM \rightarrow LM$.

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The Nature of Adsorbed Films of Caesium on Tungsten. Part I. The Space Charge Sheath and the Image Force

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State of thermal equilibrium in an enclosure having tungsten walls and containing caesium vapor.—In a large heated enclosure having tungsten walls and containing Cs vapor in thermal equilibrium, there are ions, electrons and atoms, with concentrations given by $n_e n_p/n_a = K$ where the equilibrium constant K can be calculated from the ionizing potential of Cs vapor. The interior of the enclosure constitutes a typical *plasma* with $n_e = n_p$. Near the walls are *space charge sheaths* in which particles of only one sign are usually present. The potential distribution of the weak fields that reach into the plasma are governed by the Debye-Hückel theory characterized by the Debye distance λ_D. The sheaths contain an excess (or deficiency) of ions and there is a corresponding sheath adsorption which is related to a negative surface tension (spreading force F) by Gibbs' adsorption equation.

Electrc image forces near plane metallic surfaces.—Still closer to the surface there is an *image force sheath* in which the distribution of ions and electrons is governed mainly by the image force $f = (e/2x)^2$. Throughout both the space charge and the image sheaths, the concentration of electrons or ions (whichever is larger) is given by $n = \exp(x_s/x)/8\pi x_s(x+x_L)^2$ where x_s, the *Schottky distance*, is $e^2/4kT$ and x_L is the *v. Laue distance* equal to $(kT/2\pi e^2 n_1)^{\frac{1}{2}}$, n_1 being the concentration at the boundary between the space charge sheath and the image sheath (corresponding to the saturation current).

Perturbation method for the study of image forces.—Within distances of a few Angstroms from the surface, the classical image force requires modification because the "effective reflecting plane" which determines the location of the image, changes its position as any given electron or ion approaches the surface. The image force for ions is thus greater than for electrons when these particles are at a given distance from the surface. A general method is devised for calculating the image force (a second approximation) acting on electrons very close to the surface. An approximate calculation of the electron distribution is made and then the *perturbations* produced by a given electron are used to determine the image force on that electron. In a modification of this method, the perturbation produced by a given electron in the distribution of neighboring electrons is considered to be characterized by a *perturbation free path* which is used to calculate the location of the reflecting plane and the resultant image force.

Application of methods to electrons with Fermi distribution.—These methods are used to calculate the image force on a given electron resulting from electrons near the surface of a metal (both inside and outside of it) which have a Fermi distribution consistent with the Poisson equation. A third approximation can then be made by considering that all of the electrons in the *Fermi sheath* are similarly acted on by an image force so that the sheath becomes much thinner than calculated by the second approximation. In Part II of this paper it will be shown that, because of the thinness of this sheath, it becomes possible to calculate the image force far more accurately by a new *displacement method* than by these two approximations. Similar image force considerations should govern all applications of the Fermi theory to concentrated electron atmospheres in which there are large concentration gradients.

WHEN caesium vapor, saturated at room temperature (about 0.001 barye) comes into contact with a hot tungsten filament, an adsorbed film of caesium is formed on the filament. The properties of such films have been quite extensively studied.[1–8] Methods have been devised for measuring ν_a, ν_p and ν_e (the rates of evaporation of atoms, positive ions and electrons) as functions of the temperature T and of σ, the number of adsorbed atoms per unit area.

Schottky[9] derived theoretically the following relation between the energies of evaporation of

[1] I. Langmuir and K. H. Kingdon, Science **57**, 58 (1923), and Phys. Rev. **21**, 380 (1923).

[2] H. E. Ives, Phys. Rev. **21**, 385 (1923); Astrophys. J. **60**, 209 (1924).

[3] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. **A107**, 61–79 (1925).

[4] J. A. Becker, Phys. Rev. **28**, 341–61 (1926).

[5] J. A. Becker, Trans. Am. Electrochem. Soc. **55**, 153 (1929).

[6] I. Langmuir, J. Am. Chem. Soc. **54**, 1252 (1932).

[7] I. Langmuir and J. B. Taylor, Phys. Rev. **40**, 463 (1932).

[8] I. Langmuir, J. Am. Chem. Soc. **54**, 2798 (1932). See especially pp. 2816–2831.

[9] W. Schottky, Ann. d. Physik **62**, 142–55 (1920).

atoms, ions and electrons and the ionizing potential of the atoms

$$U_a + U_i = U_p + U_e. \quad (1)$$

All these quantities are conveniently expressed in equivalent electron-volts, so that U_i is then the ionizing potential.

Langmuir and Kingdon[1] found experimentally that ν_p and ν_a are dependent on the electron affinity U_e of an adsorbed surface film of Cs on tungsten, and thus depend on ν_e. They concluded that the stability of the adsorbed film "is due to the fact that the electron affinity of a tungsten surface ($U_e = 4.62$ volts) is greater than that of caesium ions (ionizing potential $U_i = 3.88$ volts)."

A little later, M. v. Laue[10] showed theoretically that the concentrations of atoms, electrons and ions in equilibrium with a heated metal cannot be independent of one another, but must be so related as to give the proper degree of ionization for the vapor in accord with Saha's equation.[11]

The ease and accuracy with which the properties of caesium films may be determined experimentally renders them particularly suitable for fundamental investigations of the electrical properties of adsorbed films and of the forces acting between atoms on the surfaces of metals.

In an analysis[6, 8] of the experimental data of Dr. J. Bradshaw Taylor on the atom evaporation rate ν_a, a theory has been developed by which the forces between the adsorbed atoms (adatoms) can be calculated from the variation of ν_a with σ. This theory was based on the concept that the adsorbed film acts like a two-dimensional gas whose spreading force F (dynes cm^{-1}) is related on the one hand to ν_a by Gibbs' equation for the adsorption isotherm, and on the other hand to $f(r)$, the law of force between adatoms, by the Clausius virial equation. The results indicated that the adatoms behave as dipoles of moment M oriented with their axes normal to the surface, the positive end facing outward. The force of repulsion between adatoms at a distance r is thus $f = (3/2)M^2 r^{-4}$. The moment M varies with the surface concentration σ because of the depolarizing force produced by neighboring adatoms.

From these values of M, by means of the Boltzmann and the Saha equations, values of ν_e and ν_p as functions of T and σ were obtained and were found to agree well with those given by the experiments.

Although this agreement may be regarded as justification of the use of the Gibbs and Clausius equations in the treatment of this problem, there are several theoretical questions that need more careful analysis. For example, the adsorbed film of caesium was assumed to be a monatomic film with all the adatoms in one plane. This raises the question as to the distribution of atoms, ions and electrons in the space near the metal surface. Are the adsorbed atoms all on the surface or do they constitute a miniature atmosphere extending some distance from the surface?

Since the distribution of electrons within the metal and close to its surface follows the Fermi rather than the classical distribution law, any accurate calculation of the forces acting between the adatoms and the underlying metal is a difficult problem in quantum mechanics. At distances from the surface only slightly greater than atomic dimensions, the laws of quantum mechanics rapidly approach those of the classical theories.

The object of the present paper is to analyze the conditions of equilibrium between electrons, ions and atoms of an alkali metal vapor in an enclosure bounded by metallic walls. At large distances from the walls the conditions resemble those of the Debye-Hückel theory of electrolytes. Then there is a region where space charge is the dominant factor. Still nearer the metallic surface the distribution is governed by the image force. Extremely close to the surface space charge again becomes important, but in this region the quantum rather than the classical laws are applicable.

By this procedure of deriving knowledge of conditions near the surface from our more certain knowledge of the regions far from the surface, we shall avoid many of the difficulties that would be involved in an attempt to treat the surface conditions directly.

I. State of Thermal Equilibrium in an Enclosure

Consider an enclosure containing alkali metal vapor in thermal equilibrium at the temperature

[10] M. v. Laue, Sitzb. Preuss. Akad. Wiss. **32**, 334–48 (1923).

[11] M. N. Saha, Zeits. f. Physik **6**, 40 (1921), and Phil. Mag. **44**, 1128 (1922).

T. Let n_e, n_p, n_a be respectively the average number of electrons, positive ions and atoms per unit volume at any given point within the enclosure.

Electrical pressure resulting from segregation

At sufficiently high concentrations of ions and electrons the electrical forces between the particles must cause deviations from the ideal gas laws. Debye and Hückel[12] have developed the theory of such forces for electrolytic solutions and their equations are applicable to ionized gases. The effect of the charges on the ions and electrons is to cause each ion to be surrounded by an increased concentration of electrons (and *vice versa*), so that the lines of force emanating from the ion do not extend to infinity but terminate within a finite distance. We shall refer to this phenomena as segregation.[13] The potential in the neighborhood of an ion, instead of falling off in proportion to $1/r$, varies in proportion to $(1/r)$ exp $(-r/\lambda)$, where the constant λ may be called the *Debye distance*. Its value, calculated by Debye and Hückel by simultaneous solution of the Boltzmann and Poisson equations, is

$$\lambda=(kT/4\pi e^2(n_e+n_p))^{1/2}$$
$$=4.896\ (2T/(n_e+n_p))^{1/2}\text{ cm}, \quad (2)$$

where k is the Boltzmann constant 1.371×10^{-16} erg deg.$^{-1}$ and e is the electronic charge 4.770×10^{-10} e.s.u. according to Birge.[14]

The total pressure p exerted by the ionized gas is then

$$p=nkT-e^2(n_e+n_p)/6(\lambda+a), \quad (3)$$

where $n=n_a+n_e+n_p$, and a is the effective distance of nearest approach of the ions and electrons, or, by combining with Eq. (2) and neglecting a compared to λ,

$$p=nkT-5.476\times10^{-21}(n_e+n_p)^{3/2}T^{-1/2}\text{ barye}. \quad (4)$$

The first term in the right-hand member of Eq. (3) corresponds to the ideal gas law while the second term represents what may be called the *electric pressure*. As n_e+n_p increases, the total pressure rises at first in proportion to n, but then more slowly until at a certain value $(n_e+n_p)_M$ the pressure reaches a maximum value p_M. We then have

$$(n_e+n_p)_M=4(kT)^3/\pi e^6=2.786\times10^8T^3\text{ cm}^{-3}. \quad (5)$$

By analogy with van der Waal's theory of the transition from the gaseous to liquid states, we may conclude that just before n_e+n_p reaches the value $(n_e+n_p)_M$, the electric forces should make the gas phase unstable so that a *condensed phase* should appear in which there is a far higher concentration than given by $(n_e+n_p)_M$. From Eq. (5) we see, however, that with temperatures of the order of 1000°K such instability would occur only when the concentration of ions and electrons becomes about 3×10^{17} cm^{-3}, while for all concentrations below about 10^{15} the effect of the electric pressure may be neglected.

Very close to a metal surface, because of the electric image force, the concentrations of ions and electrons may reach values as great as 10^{17}, so that from the foregoing considerations we might expect a condensed phase to appear. We shall see, however, that other factors make this improbable unless negative ions are also present.

Equilibrium constants

At concentrations so low that the electric pressure is negligible, the law of mass action gives

$$K_n=n_en_p/n_a, \quad (6)$$

where K_n, the equilibrium constant for any given vapor, is a function only of temperature. The value of K_n as a function of temperature is found[15] to be

$$K_n=(\omega_e\omega_p/\omega_a)[(2\pi m_ekT)/h^3]$$
$$\times\exp(-U_{i0}e/kT), \quad (7)$$

where U_{i0} is the ionizing potential of the alkali atom at the absolute zero and the ω's are the statistical weights of the normal states of the free electrons, ions and atoms. For the vapors of the alkali metals these have the values $\omega_e=\omega_a=2$ and $\omega_p=1$. Inserting Birge's numerical values[14] for m_e, k and h, and expressing the concentration in terms of cm^{-3}, we obtain

$$K_n=2.447\times10^{15}T^{3/2}\exp(-11606U_i/T), \quad (8)$$

[12] P. Debye and E. Hückel, Phys. Zeits. **24**, 185–206 (1923), and P. Debye, ibid. **25**, 97–107 (1924); see also A. A. Noyes. J. Am. Chem. Soc. **46**, 1080–97 (1924).

[13] See a paper entitled *Forces near the Surfaces of Molecules*, I. Langmuir, Chem. Rev. **6**, 451–79 (1929), especially pp. 459–60.

[14] R. T. Birge, Rev. Mod. Phys. **1**, 1 (1929).

[15] R. H. Fowler, *Statistical Mechanics* (1929), p. 281.

where U_i is measured in volts. For convenient calculation this may be written,

$$\log_{10} K_n = 15.3886 + (3/2)\log_{10} T - 5040 U_{i0}/T. \quad (9)$$

The ionizing potentials of the alkali metals can be accurately calculated from the $1S$ terms in the spectrum. Taking the wave numbers given for these terms by Franck and Jordan[16] and dividing by 8106 as given by Birge,[14] we obtain the following values of U_{i0} expressed in volts: Cs, 3.874; Rb, 4.155; K, 4.318; Na, 5.113 and Li, 5.364.

There are several other possible definitions of the equilibrium constant.[17] One in very common use is

$$K_p = p_e p_p / p_a \quad (10)$$

where p_e, p_p and p_a are the partial pressures of electrons, ions and atoms. Since $p = nkT$,

$$K_p = kTK_n. \quad (11)$$

In experiments with tungsten filaments in alkali metal vapors, we do not measure n or p directly, but determine the rate at which atoms, ions or electrons strike the filament surface or evaporate from it. Let μ_e, μ_p and μ_a be the number of electrons, ions or atoms per unit time per unit area that cross any given imaginary surface in the gas. Classical kinetic theory then gives

$$\mu = p(2\pi mkT)^{-1/2} = n(kT/2\pi m)^{1/2}. \quad (12)$$

For electrons[14] $m_e = 9.035\times10^{-28}$g, so that

$$\mu_e = 1.554\times10^{5} n_e T^{1/2}, \quad (13)$$

while for ions of molecular weight M (0 atom $=16$), $m_p = 1.649\times10^{-24}M$ gram, giving

$$\mu_p = 3637 n_p (T/M)^{1/2}. \quad (14)$$

This may also be used for calculating μ_a.

In terms of the pressure p_a (in baryes)

$$\mu_a = 2.653\times10^{19} p_a (MT)^{-1/2}. \quad (15)$$

The rates of flow of electrons and ions to any metallic electrode are directly measurable as current. The current density I in amperes cm^{-2} is thus

$$I = e\mu = 1.591\times10^{-19}\mu. \quad (16)$$

Even the rate of flow of alkali metal atoms, μ_a, can be measured as a current I_a by heating a filament to such high temperature that all atoms which strike it are converted to ions. We thus have two other useful equilibrium constants:

$$K_\mu = \mu_e\mu_p/\mu_a \quad \text{and} \quad K_I = I_e I_p / I_a. \quad (17)$$

The relations between these "constants" are

$$K_\mu = (kT/2\pi m_e)^{1/2} K_n = 1.554\times10^{5} T^{1/2} K_n, \quad (18)$$

$$K_I = eK_\mu = 2.472\times10^{-14} T^{1/2} K_n \text{ amp. cm}^{-2}. \quad (19)$$

Potential distribution

Since the relative numbers of electrons and ions emitted by the walls of the enclosure depend on the material of the walls, n_e and n_p are not always equal and therefore there will be a space charge $\rho = e(n_p - n_e)$.

The potential distribution is related to ρ in accordance with Poisson's equation $\Delta V = -4\pi\rho$.

In a state of thermal equilibrium and at concentrations so low that the electrical pressure is negligible, the distribution of ions and electrons is given by the Boltzmann equations,

$$n_e = n_0\epsilon^{\eta}, \qquad n_p = n_0\epsilon^{-\eta}, \quad (20)$$

where η is a dimensionless parameter proportional to V defined by

$$\eta = Ve/kT = 11600\,V/T \quad (21)$$

if V is measured in volts. The zero of potential is taken to be that which makes $n_e = n_p = n_0$.

The value of n_0 is readily obtained from Eq. (6) by placing $n_e = n_p = n_0$ so that

$$n_0^2 = n_a K_n. \quad (22)$$

If with any given value of n_0 the enclosure is made of sufficiently large size, n_e and n_p will be practically equal throughout the enclosure except near the walls. If we neglect, for the present, forces acting on the ions or electrons due to the charges they induce individually on the walls (image force), we find that the potential distri-

[16] J. Franck and P. Jordan, Handb. d. Physik, Berlin **23**, 703 (1926).

[17] Much of the nomenclature used in the present paper and some of the methods of reducing non-equilibrium conditions to equilibrium were introduced in connection with a study of the dissociation of hydrogen into atoms, I. Langmuir, J. Am. Chem. Soc. **38**, 1145-56 (1916).

bution near any plane bounding surface is given[18] by

$$x=\lambda_0 \ln (\tanh (\eta_1/4)/\tanh (\eta/4)) \quad (23)$$

where λ_0 is the Debye distance obtained from Eq. (2) by putting $n_e=n_p=n_0$, and x is the distance from the wall to any point whose potential is V. The value of η_1 is found by substituting $V=V_1$ in Eq. (21), V_1 being the potential at the wall ($x=0$).

Expansion of Eq. (23) gives

$$x/\lambda_0=\ln \tanh (|\eta_1|/4)-\ln (|\eta|/4) +(1/48)\eta^2-(7/23040)\eta^4+\cdots. \quad (24)$$

In all the cases that are of interest to us $|\eta_1|\gg 1$. For small values of η, that is, when $\eta^2<1$, we may neglect the first term of the second member of Eq. (24) so that the equation reduces to

$$|\eta|=4\epsilon^{-x/\lambda_0}. \quad (25)$$

The potential thus falls to $1/\epsilon$th value for each increment of x equal to the Debye distance λ_0. The potential and the concentrations become uniform at a distance from the wall which is a small multiple of λ_0.

When $\eta^2\gg 1$, Eq. (20) shows that there are particles of only one sign present.

We see that there are two rather distinct regions to be considered. In the interior of the enclosure where $\eta^2<1$, and n_e is approximately equal to n_p, we have a typical *plasma*[19] in which there are only weak fields and the logarithm of the potential varies linearly with distance in accord with Eq. (25). Close to the walls where $\eta^2>1$ are typical *sheaths* where there are strong space charges due to charged particles which are all of the same sign. These sheaths, however, differ from those near collectors in gaseous discharges in that here, under the equilibrium conditions that prevail, there are present the trapped electrons (or ions) necessary to give the complete Maxwell-Boltzmann distribution. This produces an extremely rapid change in potential very close to the walls.

Potential and concentration in the space charge sheath

Since within the sheath particles of one sign predominate, we may conveniently omit the subscripts p and e in designating the concentration and use n to represent the concentration of the particles which are present in excess while n' is used for the particles present only as a minority. Thus by Eq. (20) we have

$$n=n_0 \exp (|\eta|), \quad n'=n_0 \exp (-|\eta|) \quad (26)$$

and

$$nn'=n_e n_p=n_0^2. \quad (27)$$

We may let n_1 be the value of n at the surface of the electrode, i.e., at $x=0$. The value of n_1 depends on the electron emission or the positive ion emission (whichever is larger) from the metal surface, in accord with Eqs. (13) or (14).

Eq. (23) may now be put in a more convenient form by substituting a new variable defined by

$$u=\exp (-|\eta|/2)=(n_0/n)^{1/2}. \quad (28)$$

We thus obtain for $u<1$

$$\ln \tanh (\eta/4) =\ln \frac{1-u}{1+u}=-2\left(u+\frac{u^3}{3}+\frac{u^5}{5}+\cdots\right). \quad (29)$$

If $(1/3)u^2$ can be neglected compared to unity, each member of Eq. (29) equals $-2u$ and thus Eq. (23) reduces to

$$x+x_L=2\lambda_0 u=2\lambda_0(n_0/n)^{1/2}, \quad (30)$$

where x_L is a parameter having the dimensions of a length, which we may call the *v. Laue distance.* Its value is

$$x_L=2\lambda_0 u_1=2\lambda_0(n_0/n_1)^{1/2}. \quad (31)$$

If we introduce the value of λ_0 as given by Eq. (2) these equations may be written

$$x+x_L=(kT/2\pi e^2 n)^{1/2}=9.792(T/n)^{1/2}\ \text{cm}, \quad (32)$$

$$x_L=(kT/2\pi e^2 n_1)^{1/2}=9.792(T/n_1)^{1/2}\ \text{cm}. \quad (33)$$

These equations give the distribution of the concentration n within the space charge sheath. The concentration n' of the minority particles is readily calculated by Eq. (27) from n_0 as given

[18] Equations equivalent to Eq. (23) have been derived for electrolytic solutions by K. F. Herzfeld, Phys. Zeits. **21**, 28 (1920), and for ionized metal vapors by M. v. Laue, Preuss. Akad. Wiss. Berlin, Ber. **32**, 334–48 (1923), see p. 340; Handb. d. Radiologie **VI**, 472–8 (1925); R. H. Fowler's *Statistical Mechanics*, Cambridge Univ. Press (1929), p. 283.

[19] I. Langmuir, Phys. Rev. **33**, 954–89 (1929). See particularly pp. 964, 979, 980.

by Eq. (22). The potential distribution is given by Eq. (26). The 3d column of Table I gives the values of x_L for a series of values of n_1.

Within the *plasma* the potential distribution is given by Eq. (25) while within the *sheath* it may be obtained from Eq. (32). Although the boundary between these two regions is of course not sharp, there is a narrow region in which both Eqs. (25) and (32) are approximately fulfilled. Thus if we place $|\eta| = 1.5$ (or $V = \pm 1.3 \times 10^{-4} T$ volts) we find that Eq. (25) gives $x = 0.98\lambda_0$, and Eqs. (30) and (28) give $x = 0.945\lambda_0$, while the rigorous Eq. (23) gives $x = 1.026\lambda_0$.

Sheath adsorption

If the radius of curvature for all parts of the surface of the enclosure is large compared to λ_0, we may look upon the ionized gas as constituting a field-free and electrically neutral plasma except within plane sheaths covering the walls. These sheaths have many properties which may profitably be considered as belonging to the metal surface which they cover. For example, the excess or deficiency of ions integrated throughout the thickness of the sheath is a part of the total adsorption by the metal surface. There is also a surface free energy or negative surface tension associated with the sheath which, in thermodynamical calculations, is to be included in the spreading force F of the adsorbed film on the surface. For such purposes, of course, the effects due to the fields extending into the plasma for distances several times λ_0 should be included with those in the sheath proper.

Let σ_s be the total amount per unit area of *adsorbed* material in the form of positive ions within the sheath, so that

$$\sigma_s = \int_0^\infty (n_p - n_0) dx.$$

Inserting the value of n_p from Eq. (20) and expressing dx in terms of η by differentiating Eq. (23) we obtain

$$\sigma_s = 2n_0\lambda_0(\epsilon^{-\eta_1/2} - 1). \qquad (34)$$

If we replace η_1 in this equation by η, σ_s becomes the total amount adsorbed per unit area in that part of the sheath which lies between the plasma and the plane at which the potential corresponds to η. Eliminating η by means of Eq. (20) and inserting the value of λ_0 from Eq. (2) we get

$$\sigma_s = (kT/2\pi e^2)^{1/2}(n_p^{1/2} - n_0^{1/2}). \qquad (35)$$

If the potentials in the sheath are positive, $n_p < n_0$ and there is, according to Eq. (34), a negative adsorption in the sheath which cannot exceed $2n_0\lambda_0$. With negative sheath potentials, however, the positive ion adsorption is positive and rapidly becomes equal to $4n_0\lambda_0^2/x_L$. In this case it can be shown by Eqs. (34), (28), (30) and (31) that half of the total amount adsorbed within the sheath lies within the distance x_L of the surface.

Surface tension in the sheath

M. v. Laue[20] has calculated the surface tension resulting from an electron sheath on the surface of a hot metal. For this purpose he adds the total energy of the electrostatic field per unit area to the total force per unit length exerted by the electron atmosphere on a plane perpendicular to the sheath. These two effects contribute equally to the resulting surface tension.

Carrying through a similar calculation for the sheaths produced with ionized metal vapor that we are now considering, we obtain rigorously

$$U_s = [(kT)^{3/2}/e(2\pi)^{1/2}][n_p^{1/4} - n_e^{1/4}]^2 \qquad (36)$$

or

$$U_s = 1.342 \times 10^{-15} T^{3/2}(n_p^{1/4} - n_e^{1/4})^2 \text{ erg} \cdot \text{cm}^{-2}, \qquad (37)$$

where U_s is the total electrostatic energy per sq. cm between the interior of the plasma and the plane at which the ions and electrons have the concentrations n_p and n_e. Since the *pressure* of the electrons and ions (in excess over that in the plasma) contributes an equal part, the surface spreading force is

$$F = 2U_s. \qquad (38)$$

If $n_e \gg n_p$, the value of F is the same as that given by the equation derived by v. Laue.

Comparison of F and σ_s by Gibbs' equation for adsorption

The general statement of Gibbs' law for the

[20] Max v. Laue, Jahr. d. Radioakt. **15**, 238 (1918).

adsorption isotherm[21] is

$$dF/d\ln a=\sigma kT, \tag{39}$$

where F is the spreading force, a is the activity of the adsorbed vapor in the gaseous phase in equilibrium with the solid, and σ is the number of atoms adsorbed per unit area. The derivative $dF/d\ln a$ represents the rate of change of F when $\ln a$ is changed by altering the concentration in the gas phase while the surface area of the adsorbing surface is kept constant.

This equation should be applicable to the values of F and σ_s which we have obtained in Eqs. (35), (36) and (38). Let us eliminate n_p by Eq. (20) and thus obtain

$$F=2kTB(n_0^{1/2}-n_e^{1/2})^2, \tag{40}$$

$$\sigma_s=B[n_0-(n_e n_0)^{1/2}], \tag{41}$$

where

$$B=(kT/2\pi e^2 n_e)^{1/2}=9.792T^{1/2}n_e^{-1/2}. \tag{42}$$

In these equations n_e represents the electron concentration at the metal surface, or rather at a distance from the surface at which the image force is negligible.

Let us now consider a case in which n_e is determined by the electron emission characteristic of the material of the walls unaffected by the presence of adsorbed films which might alter the contact potential. This condition can readily be realized at high temperatures, and particularly with metals having high electron emissivity which have little tendency to adsorb ions.

Eq. (39) can be written

$$\ln a=\int dF/\sigma_s kT. \tag{43}$$

Inserting the values of F and σ_s and integrating, taking n_e to be constant, we obtain for all values of n_0

$$a=\text{const.}\times n_0^2=\text{const.}\times n_a. \tag{44}$$

Thus we see that the values of F and σ_s are consistent with Gibbs' equation. The activity a is proportional to the concentration n_a of atoms. This result is in accord with the ordinary use of Gibbs' equation. Since in all practical cases n_0 is negligibly small compared to n_a, the degree of ionization in the plasma is not enough to influence the activity a. In Langmuir and Kingdon's[3] previous use of the Gibbs' equation, they erroneously took the activity to be proportional to n_p and were thus led to draw the incorrect conclusion that under certain conditions caesium adatoms attracted one another.

[21] Thermodynamics by Lewis and Randall, McGraw-Hill (1923), pp. 250 and 251.

II. Conditions at Plane Metallic Surfaces. Electric Image Forces

The essential characteristic of metallic conductivity is that no steady electrostatic field can be maintained within the conductor except by the continual expenditure of energy. Under equilibrium conditions the surface of any metal must be an equipotential surface. If an electric field E exists outside the metal so that lines of force reach the metal surface, the direction of the field at the surface must be normal to the surface, and since these lines must terminate at the surface, there must be a surface charge s given by $E=-4\pi s$.

Potential distribution

The potential distribution in a region containing space charges near a plane conducting surface is ordinarily calculated by Poisson's equation

$$d^2V/dx^2=-4\pi\rho \tag{45}$$

together with the boundary condition $V=$ constant over the conducting surface. The electric force acting on any electron is then $e\,dV/dx$ (or $-e\,dV/dx$) for a positive ion of charge $+e$).

This method, which considers a continuous distribution of charge, is strictly justifiable only if the effects due to the discrete nature of the electric charges are negligible.

The obvious need, under certain conditions, for modifications in the theory to take into account the actual discontinuous distribution, has led to frequent confusion, to numerous errors and to much discussion. It seems worth while, therefore, to examine rather critically the nature of the forces acting on electrons or ions which are close to ideal metallic surfaces (equipotential surfaces).

In free space the potential at distance r from a point charge e is e/r; but if this point charge lies at a position A close to a semi-infinite mass of metal bounded by an equipotential plane sur-

face S, the potential at any point P outside the metal is equal to $(e/r)-(e/r')$. Here r is the distance from P to A', where A' is the electric image of A in the surface, A and A' being symmetrically located with respect to S. Thus with any number of charged particles the potential at P is

$$V=\Sigma(e/r)-\Sigma(e/r'). \tag{46}$$

A term corresponding to the image potential is absolutely necessary in order that S may be an equipotential surface. It is, however, equally possible to write the equation in the form

$$V=\Sigma(e/r)+\int ds/r_s, \tag{47}$$

where s represents the surface charge density at any point on the surface whose distance from P is r_s. The integration is to be carried over the whole surface S.

Since the charged particles to be considered are moving rapidly (velocities negligible compared to light), it is obvious that the potential V at any point will fluctuate with time. The value of V given by Eq. (46) is thus to be regarded as an instantaneous value corresponding to any given instantaneous positions of the particles. We can use such values of V to calculate the instantaneous force which the *potential field* would exert on a small charge placed at the position P, but must be careful not to use these fluctuating values of V to calculate changes in the energies of a charged particle at different times. For example, in general it will not be true that $\Delta Ve=\Delta(\frac{1}{2}mv^2)$.

This use of Eq. (46) theoretically gives a complete general solution for the potential distribution and should be used whenever the detailed effects of the discontinuous distribution are to be taken into account. However, we ordinarily do not know the instantaneous positions of all the charged particles: we know only certain average values of the concentrations. The problem of greatest present interest to us is to determine how the concentration n of electrons or ions varies close to a metallic surface. We need then to adopt a suitable definition of n.

Jeans[22] discusses the relative merits of several definitions for the density of a gas. If the distribution of matter were continuous, the density would normally be defined as the limiting value of m/v, the ratio of mass to volume, as v shrinks to infinitesimal size. But with a discontinuous distribution the limit of m/v is zero for all elements of volume except those containing a particle, and is infinite for the latter.

With an infinite quantity of a homogeneous gas consisting of molecules, the density could be defined as the limiting value of m/v as v is increased indefinitely.

For gases which are neither continuous nor homogeneous, Jeans finds it impossible to choose a rigorous definition but adopts as a practical one the ratio m/v in which v is taken of such size that it "may, without appreciable error, be supposed to be infinitely great in comparison with the distance between neighboring molecules, and at the same time infinitely small compared with the scale of variation of density of the gas." Very close to a metal surface we shall see that the density may vary enormously within distances far less than the average distance between neighboring molecules, so that Jeans' definition of density becomes meaningless.

We are, however, interested primarily in systems in equilibrium which are not assumed to be undergoing any progressive change with time. The difficulties of Jeans' definitions are thus completely avoided if we adopt Fowler's[23] suggestion that *time averages* instead of space averages be used. Thus if v is a small volume enclosing the point P, and N is the number of electrons within v at any given time t, we may define n as the limiting value of $[\int_0^t(N/v)dt]/t$ as we let t approach infinity and then make v infinitesimally small.

The probability that a particle will occur at any instant of time within dv is thus $n\,dv$. As an alternative definition of n we may say that n is the *probability per unit volume* for the occurrence of an electron at P. We see then that n varies continuously throughout space, although at each instant the distribution of charge is discontinuous.

Similarly in dealing with other properties which characterize assemblies of electrons and

[22] J. H. Jeans, *Dynamical Theory of Gases*, Cambridge, 2nd Edition (1916), p. 14.

[23] R. H. Fowler, *Statistical Mechanics*, Cambridge (1929), p. 8.

ions in equilibrium, we should deal with time averages. Thus in the Boltzmann equation[24] $n=n_0\epsilon^{Ve/kT}$, both n and V are time averages and are not instantaneous values or local values.

We have seen that Eq. (46) enables us to calculate the instantaneous potential V for any given distribution of charged particles near a surface. If, however, we use this equation to find the time average potential $\bar{V}$ in a series of successive intervals, it becomes

$$V=\int ne\,dv/r-\int ne\,dv/r' \qquad (48)$$

where the first integral extends through the space outside the metal, while the second covers the corresponding hypothetical space on the other side of S.

This equation is, however, exactly equivalent[25] to Poisson's equation with $\rho=ne$, and with the boundary condition $\bar{V}=0$ at the surface S.

Therefore we are justified in using the Poisson equation alone, instead of Eq. (46) or (47), whenever we wish to know merely the average potential $\bar{V}$.

There is thus no need to take into account the discrete nature of the charged particles in calculating the potential distribution for use in connection with the Boltzmann equation. This is *true even though the average distance between the charged particles is large compared to the distance of the particles from the surface of the metal.*[26]

We shall have occasion to consider the discontinuous distribution of space charge in determining the conditions under which the ideal gas laws may be applied to concentrated space charges very close to metal surfaces.[27]

Forces acting on an electron

A single electron located at a point A, at a distance x from a plane conducting surface S, is acted on by a force $e^2/4x^2$ drawing it toward the surface. This force is equal to that which would be exerted on the electron at A by an equal positive charge at the image A' and is therefore usually called the image force.

Let us now consider the force acting on an electron B in an ionized gas close to a plane metallic surface. We have seen in the foregoing section that the average potential V at any point P can be calculated from n by Poisson's equation. It should be noted, however, in this calculation that *no electron was assumed to be located at P*, that is, the probability per unit volume for the occurrence of an electron at P was taken to be the same as at other points in the neighborhood of P.

In order to calculate the force on the electron B we must now consider that the electron is definitely located at P. This introduces an unsymmetrical element which was entirely absent in our calcuation of n and V as average values. At P, the probability of the presence of an electron now becomes unity so that $n=\infty$ at this point. In a similar way $V=-\infty$ at P. It is customary to avoid this difficulty by ignoring the presence of the electron at P in calculating V. The force acting on the electron at P is then taken to be $e\,dV/dx$.

Although we can ordinarily properly ignore the effect of the electron at P in calculating, by means of Poisson's equation, the forces resulting from the action of all the other electrons and ions, it is clear that in this way we do not allow for the image force[28] corresponding to the image at P'.

[24] R. H. Fowler, *Statistical Mechanics* (1929), see pp. 48 and 188.

[25] See Handb. d. Physik **12**, 375 (1927).

[26] R. S. Bartlett in a recent paper, Phys. Rev. **37**, 959–69 (1931), especially on pages 958 and 969, questions the validity of Poisson's equation when used in this way. He seems to think that Poisson's equation is applicable accurately only when the distance between neighboring electrons, $n^{-1/3}$ (?) is small compared to x, the distance to the surface S. Failure to distinguish between instantaneous and average values of V has probably led to this conclusion.

[27] Methods of calculating the magnitude and the frequencies of the potential fluctuations in ionized gases have been discussed by I. Langmuir, Proc. Nat. Acad. Sci. **14**, 628–37 (1928), especially pp. 632–4. See also L. Tonks and I. Langmuir, Phys. Rev. **33**, 195–210 (1929).

[28] In M. v. Laue's paper dealing with the potential distribution resulting from electron space charges in equilibrium with metal surfaces (Jahrb. d. Radioak. und Electronik **15**, 207 (1918)) he ignored the image force in some problems where this force is of vital importance. In a subsequent paper (ibid. **15**, 302 (1918)) he attempted to justify this omission by arguing that the ordinary space charge treatment includes the effect of the images. Schottky (Phys. Zeits. **20**, 220 (1919)) pointed out that this conclusion is justified for the images of all the electrons *except that of the electron on which the force is acting.* Later

Fowler[29] shows that a rigorous calculation of the distribution of electrons and ions near a surface would involve an averaging of the effects of all movable charges in the "assembly," including those within the metal. Since "such a procedure seems to be far beyond our resources at present, a correction is necessary for the polarizing effect of the individual ion (or electron) on the metal surface." A consideration of the image force $e^2/4x^2$ which constitutes just such a correction should give accurate results whenever we are justified in regarding the metal surface as an equipotential plane surface.

The forces acting on a given electron at P are of three types:

Type 1. The force $e(dV/dx)$ due to the *potential field* V as given by Eq. (48), or by Poisson's equation, from values of n_e and n_p obtained by ignoring the presence of the electron at P. Since n_e and n_p will be uniform over any plane parallel to S, Poisson's equation takes the form

$$d^2V/dx^2 = 4\pi e(n_e - n_p). \qquad (49)$$

Type 2. The *electric image force* $e^2/4x^2$ corresponding to the image at P'.

Type 3. The force that results from the *segregation of electrons* (or ions) in the neighborhood of P in accord with the Debye-Hückel effect. This force must also include that due to the *image of the segregation*. Because of this image effect, the displacements of the charges produced by the presence of the electron at P will not have spherical symmetry about P.

This rather arbitrary separation of the force into 3 parts has the advantage that it throws the whole difficulty of the calculation into the third part. If it can be shown under any given conditions that the forces due to segregation are negligible, the problem can usually be readily solved.

Potential and motive

Much confusion can be avoided by analyzing a little more closely the concept of electric potential when used to calculate the forces acting on an electron.

The general concept of potential (Newtonian) is that of a scalar quantity whose gradient is used to represent a vector field having no curl. We ordinarily conceive of a static electric field as a state of space which acts on a particle having a charge e to produce a mechanical force F which is proportional to e.

In order not to disturb unduly the distribution of neighboring charges, it is customary to postulate that the charge used to measure any given electric field shall be small.

Logically, therefore, the field intensity E should be measured by dF/de for $e=0$. This definition is consistent with common usage in all ordinary cases.

The electric image force $e^2/4x^2$ which acts on an electron or ion near a plane conducting surface varies in proportion to the square of the charge and thus the value of dF/de is zero for $e=0$. The image field which acts on the electron differs radically from ordinary electric fields in that its existence depends upon the presence of the electron upon which it acts. It is important to recognize clearly this distinction between these two types of field.

The vector field corresponding to the ordinary electrostatic field ($E=dF/dx$ for $e=0$) may be represented by the potential V. We may consider either the *instantaneous potential* V or the *average potential* $\overline{V}$. In the former case V can be determined by Eq. (46) or by Laplace's equation which must hold everywhere except inside of the electrons. The average potential $\overline{V}$ at a point P, which is usually of more interest to us, can be determined by Eq. (48), or by Poisson's Eq. (49), from the average values of n_e and n_p, excluding any effects due to the presence of an electron at P.

The image force which acts on an electron at any point P, because of the presence of any neighboring conductor, varies in magnitude and direction as P is moved throughout the available space. Thus the image force also corresponds to a vector field. Under equilibrium conditions this field will have no curl and may therefore be represented by a potential. However, this potential has very different characteristics from either V or $\overline{V}$. For example, it will not satisfy Laplace's equation, and if it is substituted into Poisson's

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v. Laue (Sitzber. Preuss. Akad. d. Wiss. **32**, 340 (1923)) acknowledged the correctness of Schottky's criticism and added an excellent discussion of the true character of the image force.

[29] R. H. Fowler, *Statistical Mechanics* (1929), p. 283.

equation in order to calculate the space charge, values of ρ or n are found which are purely fictitious, having no relation to actual space charges present.

To avoid confusion it seems desirable to adopt different terminology in describing these various kinds of potential. It seems useful to reserve the term *potential*, in electrical problems, to represent the fields which may be supposed to exist in space independently of the presence of a charge on which they act. It has been proposed[30] that the potential of the vector field corresponding to the forces which act on an electron or ion be named the *motive*, as an abbreviation of what the electrochemist calls "electromotive force." The motive M is thus defined as a scalar quantity whose gradient in any direction and at any point represents the force component per unit charge which must be applied to an electron or ion to hold it in equilibrium at the given point. Thus each particle tends to move towards a point where the motive is a minimum.

The force F_e exerted by the motive field on an electron at the distance x from a plane conducting surface is thus

$$F_e = -dMe/dx = e(dV/dx) - e^2/4x^2, \quad (50a)$$

while on a univalent positive ion the force would be

$$F_p = -dM_p/dx = -e(dV/dx) - e^2/4x^2. \quad (50b)$$

By integration we thus obtain for an electron

$$M_e = -V - (e/4x) = -V - 3.575\times10^{-8}/x \text{ volts} \quad (51a)$$

and for a positive ion,

$$M_p = +V - (e/4x) = +V - 3.575\times10^{-8}/x \text{ volts}. \quad (51b)$$

In these equations e represents the numerical value of the electron charge, i.e., e is always taken to be positive.

The motive thus consists of two parts: one being the ordinary potential V and the other the *image motive* $-e/4x$. It should be noted that with the image motive no distinction need be drawn between instantaneous and average values for they are identical. Since, however, there are these two kinds of potential, we must also distinguish between instantaneous and average values of the total motives M_e and M_p.

The essential differences between the image motive and the potential result from the fact that the former owes its origin to a displacement of electrons in the metal by the action of the electron at P. The fields set up by the segregation of electrons and ions around given ions in ionized gas, according to the Debye-Hückel theory, are clearly *motive fields* and not potential fields, since they also depend for their existence on the definite presence of a charged particle at a given point. We see then in accordance with our classification of the forces acting on an electron at a point P into 3 types, that the motive M_e will consist also of three parts: the *potential* $-V$, the *image motive* $-(e/4x)$ and the "*segregation motive.*"

Distribution of electrons and ions

Since the work done in moving a charged particle from one place to another is determined by the motive instead of the potential, it is clearly the motive that should occur in the exponent of the Boltzmann equation. Making this modification in Eq. (20) and introducing the value of the motive from Eq. (51) we obtain

$$\left.\begin{aligned} n_e &= n_0\epsilon^{\eta}\epsilon^{x_s/x} \\ \text{and} \qquad n_p &= n_0\epsilon^{-\eta}\epsilon^{x_s/x}, \end{aligned}\right\} \quad (52)$$

where x_s is a parameter having the dimensions of a length which we may call the *Schottky distance.*[31] Its value is

$$x_s = e^2/4kT = 4.149\times10^{-4}/T \text{ cm}. \quad (53)$$

Double differentiation of Eqs. (51) and combination with Poisson's Eq. (49) gives

$$\left.\begin{aligned} d^2M_e/dx^2 &= -4\pi e(n_e - n_p + n_F), \\ d^2M_p/dx^2 &= -4\pi e(n_p - n_e + n_F), \end{aligned}\right\} \quad (54)$$

where

$$n_F = 1/(8\pi x^3) = 0.0398/x^3. \quad (55)$$

Comparison with Eq. (49) shows that the motive distribution is in accord with Poisson's

[30] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. **A107**, 68 (1925), and K. T. Compton and I. Langmuir, Rev. Mod. Phys. **2**, 152 (1930).

[31] This parameter occurs in the equations first deduced by W. Schottky, Phys. Zeits. **15**, 872 (1914).

equation only if we are willing to consider[32] a *fictitious space charge* en_F, whose effects thus replace those of the image force.

This form of expression has the advantage that it enables us to determine the relative importance of true space charge and image force (n_F) as factors determining the distribution of charged particles. If $|n_p-n_e|\gg n_F$, then the effects of the image force are negligible and our previous treatment which led to Eqs. (23) and (32) is adequate.

Since n_F increases very rapidly as x decreases, there must always be a region close to a metallic surface where n_F becomes much more important than n_p-n_e. We shall refer to this region as the *image sheath.*

Image sheath in neutral ionized gas

We may gain a clearer insight into the nature of the image sheath by considering the effect of image forces on an ionized vapor containing equal numbers of electrons and ions so that $n_e=n_p$. In this case even within the sheath there is no space charge and potential fields ($\bar{V}$) are absent so that the mathematical treatment is much simplified.

By putting $\eta=0$ in Eq. (52), the concentration of both electrons and ions is found to be

$$n=n_0\epsilon^{x_s/x}. \tag{56}$$

The excess concentration $n-n_0$ integrated between two values of x, say x_1 and x_2 gives the sheath adsorption between these planes. Let us choose both x_1 and x_2 large compared to x_s; then we may expand the exponential and by integration obtain

$$\sigma=n_0x_s[\ln(x_2/x_1)+\tfrac{1}{2}x_s(x_2-x_1)/x_1x_2+\cdots]. \tag{57}$$

If we let x_2 increase without limit, we see that the logarithmic term causes σ to approach ∞. This indicates that an image force varying inversely as x^2 falls off so slowly with increasing distance that it would cause an infinite total adsorption for a semi-infinite enclosure bounded by a plane metallic surface. This difficulty disappears if we consider the Debye-Hückel segregation. The range of the image force cannot exceed a distance comparable with the Debye distance λ given by Eq. (2).

Debye and Hückel[12] have shown that the potential at a distance r from an ion in an ionized gas is

$$V=(e/r)\exp(-r/\lambda). \tag{58}$$

The attractive force F between a positive and a negative ion (or electron) at a distance r apart is thus

$$F=e\,dV/dr=(e/r^2)(1+r/\lambda)\exp(-r/\lambda). \tag{59}$$

The plane which is perpendicular to and bisects the line connecting the ions is an equipotential surface ($V=0$) and therefore may be replaced by a metallic conductor without altering the force F. Putting $r=2x$ in Eq. (59), where x is now the distance from one ion to the plane, we have for the image force acting on an ion in a neutral ionized gas

$$F=-(e^2/4x^2)(1+2x/\lambda)\exp(-2x/\lambda). \tag{60}$$

The motive M is then found by integration to be

$$M=(e/4x)\exp(-2x/\lambda). \tag{61}$$

For small values of x this does not differ appreciably from that given by Eq. (51). The sheath adsorption σ between x and ∞ is then given by

$$\sigma/n_0=\int_x^\infty\{\exp[(x_s/x)\epsilon^{-2x/\lambda}]-1\}dx. \tag{62}$$

Although according to Eq. (2), λ is a function of n, it will remain substantially constant until x decreases to a value comparable with x_s, for by Eq. (56) n is also constant and equal to n_0 within this region.

When $x<x_s$, however, the exponent $2x/\lambda$ is very small compared to unity even after n has increased considerably, since $x_s\ll\lambda$. Thus in Eq. (62) we may take λ to be constant and equal to λ_0. If now $x\ll\lambda_0$ integration gives

$$\sigma/n_0=x_sEi(x_s/x)-x_s\ln(2.334\,x_s/\lambda_0)+x(1-\epsilon^{x_s/x}). \tag{63}$$

If we take $x\ll x_s$, which is the only region where there is appreciable adsorption, we can use the semiconvergent expansion for the

[32] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. **A107**, 69 (1925).

exponential integral Ei obtaining

$$\sigma/n_0=(x^2/x_s)\exp(x_s/x)-x_s\ln(2.33\,x_s/\lambda_0). \quad (64)$$

This equation gives the sheath adsorption caused by a plane metallic surface in contact with a neutral ionized gas, taking into account the Debye-Hückel segregation.

Let us now consider the conditions that must be fulfilled in order that $n_e=n_p$.

By dividing Eq. (13) by (14), the condition for equality of n_e and n_p is seen to be

$$\mu_e/\mu_p=42.73\,M^{1/2}. \quad (65)$$

Thus for caesium ($M=132.8$) a neutral ionized vapor occurs if the amount of adsorbed caesium is such that the electron emission is 492 times as great as the ion emission. From equations based on Taylor's experimental data[6] we find that this value of the ratio of the emissions corresponds to a film for which the contact potential V (in volts) against a clean tungsten surface is given by

$$V=2.754-2.50\times10^{-3}T+9.24\times10^{-5}T\log_{10}\mu_a, \quad (66)$$

where T is the temperature of the tungsten surface. Taylor's data give an equation[6] which expresses μ_a as a function of T and σ, and also give V as a function of σ. For any given value of T we then have three equations for determining μ_a, V and σ.

In order to get a better idea of the magnitudes of the quantities involved, let us consider an enclosure at 1000°K containing such a pressure of caesium vapor that $n_e=n_p$. Putting $T=1000$ and solving the three equations we find $\mu_a=6.1\times10^{14}$ atoms cm^{-2} sec.$^{-1}$; $V=1.621$ volts and $\sigma=8.0\times10^{13}$ atoms per cm^2 of true surface which is 22.3 percent of the surface concentration corresponding to a completely covered surface.[33] To give this value of μ_a the caesium pressure at 1000°K must be 0.0084 barye and the atom concentration is $n_a=6.13\times10^{10}$. This concentration of Cs will also be produced in an enclosure at 1000°K if this is connected to a bulb containing saturated caesium vapor at 34°C (at which temperature the pressure is 0.00465 barye) since in this case also $\mu_a=6.1\times10^{14}$.

By Eq. (9) we find at $T=1000$ that $K=2.29$ and thus by Eq. (22), placing $n_a=6.13\times10^{10}$, the concentration of electrons and of ions in the enclosure is $n_0=3.75\times10^5$. Eqs. (13), (14) then give $\mu_e=1.85\times10^{12}$ and $\mu_p=3.74\times10^9$. Corresponding to these, the electron emission is 2.9×10^{-7} and the ion emission 6.0×10^{-10} ampere cm^{-2}, currents which are easily measurable.

By an analysis[8] of the experimental data it is also possible to deduce the following properties of the caesium film (at 1000° and $\theta=0.223$). Let U be the heat of evaporation at constant pressure expressed in volts and defined in accord with the Clapeyron equation

$$U=-\frac{k}{e}\left(\frac{\partial\ln p}{\partial(1/T)}\right)_\theta=-\frac{k}{e}\left(\frac{\partial\ln\mu}{\partial(1/T)}\right)_\theta+\frac{1}{2}\frac{kT}{e}, \quad (67)$$

where $e/k=11{,}606$ degrees per volt. The data give $U_a=2.45$; $U_p=3.32$; $U_e=3.22$ volts. The ionizing potential, which has a temperature coefficient $(5/2)(k/e)$ is 4.09 volts at 1000°. These values satisfy Eq. (1). The spreading force F of the adsorbed film is 43.2 dynes cm^{-1} (of which 14.6 corresponds to the ideal two-dimensional gas law $F=\sigma kT$). The dipole moment M of the adatoms (which is related to the contact potential V by the relation $V=2\pi\sigma M$) is $M=10.87\times10^{-18}$.

For comparison with these data it is of interest to give those corresponding to very low values of σ where the atoms do not affect one another. In this case for $\sigma=0$ at 1000° we find $U_a=2.83$; $U_p=2.09$; $U_e=4.84$; $U_i=4.09$. The dipole moment is $M=16.2\times10^{-18}$.

Let us now apply Eq. (64) to calculate the adsorption within various parts of the image sheath for the case $T=1000$, $\theta=0.223$. From n_0 and T we find by Eq. (2) $\lambda_0=0.252$ cm. The Schottky distance x_s by Eq. (53) is $x_s=4.15\times10^{-7}$ cm. The total adsorption beyond $x=10^{-7}$, according to Eq. (64), amounts to only $\sigma=2.5$ ions and electrons per cm^{-2}. For $x=5\times10^{-8}$ cm this has increased to 910, and to 93,000 at $x=3\times10^{-8}$. To give the observed value $\sigma=8.0\times10^{13}$ for the total adsorbed caesium we should have to place $x=1.15\times10^{-8}$ cm.

Of course at such small distances from the sur-

[33] In Taylor's experiments 0.5 percent of the tungsten surface was found to adsorb caesium much more strongly than the rest. The values of σ and the covering fraction θ used in the present paper are those corresponding to the homogeneous part (99.5 percent) of the surface.

face the concept of image force becomes rather indefinite. Let us, however, see what results are obtained by the application of the equations we have derived and later we shall discuss what modifications are needed to take into account the special conditions very near the surface of a metal.

The attractive forces which act on the ions and which hold them on the surface as an adsorbed film must be balanced by a pressure or by repulsive forces. In the image sheath, insofar as the Boltzmann equation is applicable, the pressure gradient balances the attractive force. But the forces of attraction which hold the ions in the adsorbed film on the surface must be balanced by repulsive forces of another kind, any accurate knowledge of which must involve quantum theory. Let us assume provisionally that the image force acting on these ions is still $e^2/4x$, but that this is balanced by a repulsive force which varies inversely with a much higher power of the distance. The repulsive forces then contribute only a small part to the potential energy of the adions and for the present we shall neglect them. Then the heat of evaporation of the ions U_p is equal to the change of motive as given by Eq. (51) or (61) so that

$$U_p = e/4x = 3.58\times10^{-8}/x \text{ volts.} \qquad (68)$$

Introducing the experimental value for $U_p = 3.32$, we find $x = 1.07\times10^{-8}$ cm in fair agreement with the value 1.15×10^{-8} obtained from the total image sheath adsorption by Eq. (64).

The dipole moment M should be related to x by the relation

$$M = 2ex = 9.54\times10^{-10}x. \qquad (69)$$

Substitution of the experimental value $M = 10.87\times10^{-8}$ gives $x = 1.15\times10^{-8}$ again in good agreement with that given by Eq. (64).

According to Eq. (64) the concentration of electrons and ions should increase equally as the surface is approached. The fact that the adsorbed caesium gives a film having a contact potential of 1.62 volts against clean tungsten proves that the concentration of ions must increase faster than that of the electrons. In other words the forces acting on the ions are greater than those acting on the electrons.

At these small distances it becomes important to know the location of the surface from which x is measured. We have so far considered that the metal acts as an idealized perfect conductor with a plane surface. Actually, however, as we shall see later from a consideration of Fermi's theory and of Nordheim's theory of the distribution of electrons near a metal surface there is an electron atmosphere of high concentration extending roughly 4×10^{-9} cm out beyond the potential barrier which may be thought of as the boundary of the metal. The "reflecting plane" analogous to that of the idealized conductor is thus located at a level at which the electron atmosphere has some definite concentration.

The effect of the presence of an ion near the surface may be to raise the level of this reflecting surface under the ion whereas an electron would depress the reflecting surface.

Image sheath in unipolar gas

If the particular relation between the electron and the ion emission from the surface needed to make $n_p - n_e$ is not fulfilled, then in general the sheath will contain only particles of one sign. Beyond the range of the image force the distribution is given by Eqs. (32) and (33). We now need to consider how these equations must be modified within the image sheath.

A complete solution of the problem, which may theoretically be obtained from Eqs. (54), (55) and (52), is in general not practicable. However, by making use of the fact that $x_s \ll x_L$ under all experimental conditions, it is possible to treat the problem in a simple way. By comparing Eqs. (33) and (53) we see that

$x_s \ll x_L$ whenever

$$n_1 \ll 8(kT)^3/\pi e^6 = 5.57\times10^8 T^3 \text{ cm}^{-3}. \qquad (70)$$

This condition is practically the same as that expressed by Eq. (5) for the nonformation of a condensed phase in a homogeneous ionized gas. Thus at temperatures of the order of 1000° this relation will always be fulfilled if n_1 is small compared to 10^{17} cm^{-3}, a value far higher than can be realized experimentally.

The second column of Table I gives values of x_L/x_s calculated from Eqs. (33) and (55) for a wide range of values of n_1.

Assuming then that $x_s \ll x_L$, we see by Eq. (32) that at distances from the surface comparable

with x_s space charge effects should cause no rapid change in n. The fictitious space charge n_F, however, increases extremely rapidly, by Eq. (55), as x decreases below x_s. Thus by Eq. (54) the motive M undergoes changes which are very large compared to those of the potential. This decrease in motive, corresponding to $-e/4x$ by Eq. (51), has the effect, according to Eq. (52), of increasing the concentration n by the factor $\exp(x_s/x)$. As x decreases still further, this exponential factor should finally cause n to increase until it again exceeds n_F which varies with x^{-3}. Thus very close to the surface, within the *image sheath*, there may be a *second* or *inner space charge sheath* in which potential changes again determine the distribution of concentration.

Between the two space charge sheaths the concentration may be calculated as though no abnormal changes in potential occurred. A general equation for n is thus obtained by multiplying the value of n given by Eq. (32) by this exponential factor. In this way after introducing the value of x_s from Eq. (53) we obtain

$$n=[\exp(x_s/x)]/[8\pi x_s(x+x_L)^2]. \qquad (71)$$

This equation should be applicable within the outer space charge sheath as well as the image sheath. In our further analysis of the conditions within the image sheath, we shall determine the magnitude of the errors introduced into this equation by the approximations we have made.

Definition of n_1. We have previously defined n_1 as the value of n at $x=0$. Now that we are taking the image force into account, we see that this definition is no longer permissible for n increases indefinitely as x approaches 0. This difficulty is the same as that met in defining the saturation electron emission from a hot metal. The saturation current density I_S corresponds to that theoretically obtainable if the accelerating field is reduced to zero and yet space charge effects are not present; conditions often incompatible with one another. In accord with Eqs. (13), (14) and (16), n_1 may be defined in terms of the saturation currents as follows. For electron sheaths where I_{se} is the electron saturation current in amperes cm^{-2}

$$n_1=4.044\times10^{13}I_{se}T^{-1/2}\ \text{cm}^{-3}. \qquad (72)$$

For positive ion sheaths where I_{sp} is the ion saturation current (amperes cm^{-2})

$$n_1=1.728\times10^{15}I_{sp}(M/T)^{1/2}\ \text{cm}^{-3}. \qquad (73)$$

If we hesitate to attach a precise meaning to saturation currents where electric fields near the metal surface are unavoidable, we may logically look upon n_1 as a useful parameter (defined by Eqs. (32) and (71)) which depends only on the condition of the metallic surface.

Outer boundary of image sheath

We may take the effective boundary between the outer space charge sheath and the image sheath as the plane at x_F at which $n=n_F$, for by Eq. (54) this is the place where the image force and the actual space charge contribute equally to the motive distribution.

Putting $x=x_F$ in Eqs. (55) and (71) and eliminating n_F we get

$$x_s(x_F+x_L)^2=x_F^3\exp(x_s/x_F). \qquad (74)$$

Under conditions realizable experimentally we shall find that x_F is large compared to x_s and therefore by expanding the exponential factor we obtain the equation

$$x_F^3=x_sx_L(x_L+2x_F). \qquad (75)$$

In Table I values of x_F/x_s calculated in this way from x_L/x_s are given in the fourth column. From the data in the fifth column the actual values of x_F for any temperature are obtainable. The sixth column, which contains n_F/n_1, shows that n_F and n_1 are nearly equal so that as an approximate definition of n_1 we may say that n_1 is the value of n at a plane at which $n=n_F$, that is, at the effective limit of the range of the image force.

Inner boundary of the image sheath

We may take this effective boundary between the image sheath and the inner space charge sheath to be the plane at which n again equals n_F. Let x_{FF} be the distance of this plane from the surface. From Eqs. (55), (71), (33) and (53) we obtain

$$(x_{FF}/x_s)^3\epsilon^{x_s/x_{FF}}=(x_L/x_s)^2$$
$$=8(kT)^3/\pi e^6n_1=5.57\times10^8T^3/n_1. \qquad (76)$$

The relations between x_{FF} and other parameters characterizing the space charge and image

TABLE I. *The parameters which characterize the image sheath and the two space charge sheaths.*

1 n_1/T^3 (deg.$^{-3}$ cm^{-3})	2 x_L/x_s	3 Tx_L (cm deg.)	4 x_F/x_s	5 Tx_F deg. cm	6 n_F/n_1	7 x_{FF}/x_s	8 Tx_{FF} (deg. cm)	9 n_{FF}/T^3 (deg.$^{-3}$ cm^{-3})
10^{-10}	2.36×10^{9}	9.79×10^{5}	1.77×10^{6}	736.	0.9985	0.0181	7.51×10^{-6}	9.42×10^{13}
10^{-8}	2.36×10^{8}	9.79×10^{4}	3.82×10^{5}	159.	0.9968	0.0199	8.24×10^{-6}	7.15×10^{13}
10^{-6}	2.36×10^{7}	9.79×10^{3}	8.25×10^{4}	34.2	0.9930	0.0220	9.14×10^{-6}	5.24×10^{13}
10^{-4}	2.36×10^{6}	9.79×10^{2}	1.78×10^{4}	7.39	0.9849	0.0247	1.026×10^{-5}	3.71×10^{13}
10^{-2}	2.36×10^{5}	9.79×10	3.86×10^{3}	1.60	0.9675	0.0282	1.170×10^{-5}	2.49×10^{13}
1	2.36×10^{4}	9.79	842.	0.349	0.9334	0.0329	1.37×10^{-5}	1.56×10^{13}
10	7.46×10^{3}	3.10	395.	0.164	0.9042	0.0360	1.49×10^{-5}	1.20×10^{13}
10^{2}	2.36×10^{3}	9.79×10^{-1}	186.	7.74×10^{-2}	0.8638	0.0397	1.65×10^{-5}	8.93×10^{12}
10^{3}	7.46×10^{2}	3.10×10^{-1}	88.6	3.68×10^{-2}	0.8080	0.0443	1.84×10^{-5}	6.43×10^{12}
10^{4}	2.36×10^{2}	9.79×10^{-2}	42.7	1.77×10^{-2}	0.736	0.0502	2.08×10^{-5}	4.40×10^{12}
10^{5}	7.46×10	3.10×10^{-2}	20.9	8.67×10^{-3}	0.640	0.0583	2.42×10^{-5}	2.82×10^{12}
10^{6}	2.36×10	9.79×10^{-3}	10.5	4.36×10^{-3}	0.527	0.0699	2.90×10^{-5}	1.63×10^{12}
10^{7}	7.46	3.10×10^{-3}	5.52	2.29×10^{-3}	0.392	0.0886	3.68×10^{-5}	0.80×10^{12}
10^{8}	2.36	9.79×10^{-4}	3.10	1.29×10^{-3}	0.258	0.1259	5.22×10^{-5}	0.28×10^{12}

The quantity n_1 is the concentration of electrons or ions (per cm^3) at the surface of the metal calculated on the assumption that there is no electric image force. The v. Laue distance x_L is defined by Eq. (33); the Schottky distance x_s by Eq. (53); x_F and x_{FF} locate the outer and inner boundaries of the image sheath as given by Eqs. (75) and (76); n_F and n_{FF} are the concentrations at x_F and x_{FF}.

sheaths are illustrated in columns 7, 8 and 9 of Table I. It is seen that in spite of the enormous range of variation of n_1 of 10^{18}, the values of x_{FF} at $T=1000°$ lie within the relatively narrow range from 0.7×10^{-8} to 3.7×10^{-8} cm. Thus the inner space charge sheath can lie only within distances from the surface comparable with an atomic diameter. The last column of Table I gives the concentration n_{FF} at the distance x_{FF} from the surface. At 1000° these concentrations are of the order of magnitude of 10^{22}, comparable with that of electrons within the metal.

An analysis of the validity of these equations within such close proximity of the surface will be made in a following section.

The *motive distribution* within the space charge and the image sheath may be obtained from n as given by Eq. (71) by means of the Boltzmann equation which takes the form

$$M=(kT/e)\ln(n_0/n)$$
$$=1.984\times10^{-4}T\log_{10}(n_0/n)\text{ volts.}\quad(77)$$

The *potential distribution* within the outer space charge and image sheaths can be obtained by integration of Poisson's equation, Eq. (45), after inserting the value of n from Eq. (71). Expanding the exponential factor and taking the limits of integration to be ∞ and x we obtain[34] the convergent series

$$\eta=\eta_1-2\left(\frac{x_s}{x_L}\right)^2\left[\frac{1}{3!\,2\cdot1}\frac{x_s}{x}+\frac{1}{4!\,3\cdot2}\left(\frac{x_s}{x}\right)^2+\cdots\right],\quad(78)$$

where η_1 corresponds to the potential at the surface calculated without image force.

When $x_s/x=5$, this gives $\eta-\eta_1=-1.51\,(x_s/x_L)^2$ which by Table I is an extremely small quantity. For example, with $T=1000$, $n_1=10^{10}$, $\eta-\eta_1$ would be only $2.7-10^{-8}$ corresponding to only 2.3×10^{-9} volts. The potential changes between x_F and $0.2\,x_s$, which is far within the image sheath are thus entirely negligible.

For very large values of x_s/x greater than about 10, where the series of Eq. (78) converges too slowly, the following semi-convergent series (based on that used for the exponential integral $Ei\,x$) becomes more useful:

$$\eta=\eta_1-\tfrac{1}{3}(x_s/x_L)^2\epsilon^{x_s/x}[3!\,(x/x_s)^4+4!\,(x/x_s)^5+\cdots].\quad(79)$$

By Table I we see that x_s/x_{FF} is a quantity of the order of magnitude of 30 and thus the first

[34] In these integrations some logarithmic terms occur which become infinite when $x=\infty$. If, however, as in the derivation of Eq. (64), we take into consideration the segregation and integrate out only to a distance comparable with x_L, we find that the logarithmic terms become negligible.

term in the bracket alone is needed to calculate the potential at x_{FF}. Comparison of Eqs. (76) and (79) then gives

$$V_{FF}=V_1-(2kT/e)(x_{FF}/x_s).$$

The motive M_{FF} at x_{FF} is according to Eqs. (51) and (53)

$$M_{FF}=V_1-(kT/e)(x_s/x_{FF}),$$

so that

$$(V_{FF}-V_1)/(M_{FF}-V_1)=2(x_{FF}/x_s)^2.$$

Thus since x_{FF}/x_s is of the order of magnitude of 0.03 by Table I we see that the potential change through the whole image sheath from x_F to x_{FF} is only about 1/500th of the change in motive in the same distance. This conclusion indicates that the effects of space charge are wholly negligible within the image sheath and furnishes a justification of our derivation of Eq. (70) in which the concentration given by Eq. (32) was merely multiplied by exp (x_s/x).

III. A Perturbation Method for the Study of the Image Force

In order to understand the nature of the image force on an electron close to a metallic surface, it is important to know the effect of the electron atmosphere which must extend an appreciable distance beyond the atoms of the metal. The principles involved may be illustrated by considering the interactions of individual electrons within the space charge sheath. By application of the Fermi-Sommerfeld theory of electrons in metals and Nordheim's theory of the transmission of electrons through surface barriers, the theory may then be extended to the case of electrons very close to a metallic surface.

By combining the Poisson and Boltzmann equations in the case of an electron sheath we obtain

$$d^2\eta/dx^2=(4\pi e^2n_0/kT)\epsilon^{\eta}. \tag{80}$$

The electron distribution given by Eq. (32) represents a special solution of this equation for the boundary conditions $\eta=0$ and $d\eta/dx=0$ at $x=\infty$. The potential distribution corresponding to this case, given by

$$\exp(\eta_1)=(kT/2\pi e^2n_0)(x+x_L)^{-2}, \tag{81}$$

may be obtained by integration of Eq. (80) or from Eqs. (30), (26) and (2).

Curve I of Fig. 1 shows the potential distribution obtained from this equation for the case that $\lambda_0=1$ cm and $x_L=10^{-4}$ cm. The value of x_L is taken as the unit for expressing x. Thus the surface of the metal is located at $x=0$.

Let us now consider the effect of introducing a small surface charge uniformly distributed over a plane P located at x_P. The potential at any point instead of being η_1 will now be changed to $\eta=\eta_1+\delta$ as illustrated in Fig. 1 by curves II and III. By substituting $\eta_1+\delta$ in place of η in Eq. (80), expanding $\epsilon^{\delta}=1+\delta$, and eliminating η_1 by Eq. (81) we obtain

$$d^2\delta/dx^2=2\delta/(x+x_L)^2. \tag{82}$$

The solution of this equation is

$$\delta=A(x+x_L)^2+B(x+x_L)^{-1}, \tag{83}$$

where A and B are integration constants. The two branches II′ and III′ of the curve on opposite sides of P evidently have different values of A and B.

These perturbations in η produced by the charge at P become small at large distances. For $x>x_P$ it is clear that $\delta=0$ at $x=\infty$ and therefore by Eq. (83) $A=0$, but B can have any arbitrary small value. Thus if δ_3 represents the value of δ for $x>x_P$ (Curve III′) we have

$$\left.\begin{aligned}\delta_3&=B(x+x_L)^{-1}\\ \text{and}\qquad d\delta_3/dx&=-B(x+x_L)^{-2}.\end{aligned}\right\} \tag{84}$$

On the other side of $P(x<x_P)$, the perturbations disappear at the surface of the metal so that $\delta_2=0$ at $x=x_L$ and thus Eq. (83) gives

$$B=-Ax_L^3 \quad \text{for} \quad x<x_P,$$

whence

$$\left.\begin{aligned}\delta_2&=A[(x+x_L)^2-x_L^3(x+x_L)^{-1}]\\ \text{and}\qquad d\delta_2/dx&=A[2(x+x_L)+x_L^3(x+x_L)^{-2}].\end{aligned}\right\} \tag{85}$$

The charge on the plane P is subjected to a force per unit area or pressure p given by

$$8\pi(e/kT)^2p=(d\delta_3/dx)_P^2-(d\delta_2/dx)_P^2. \tag{86}$$

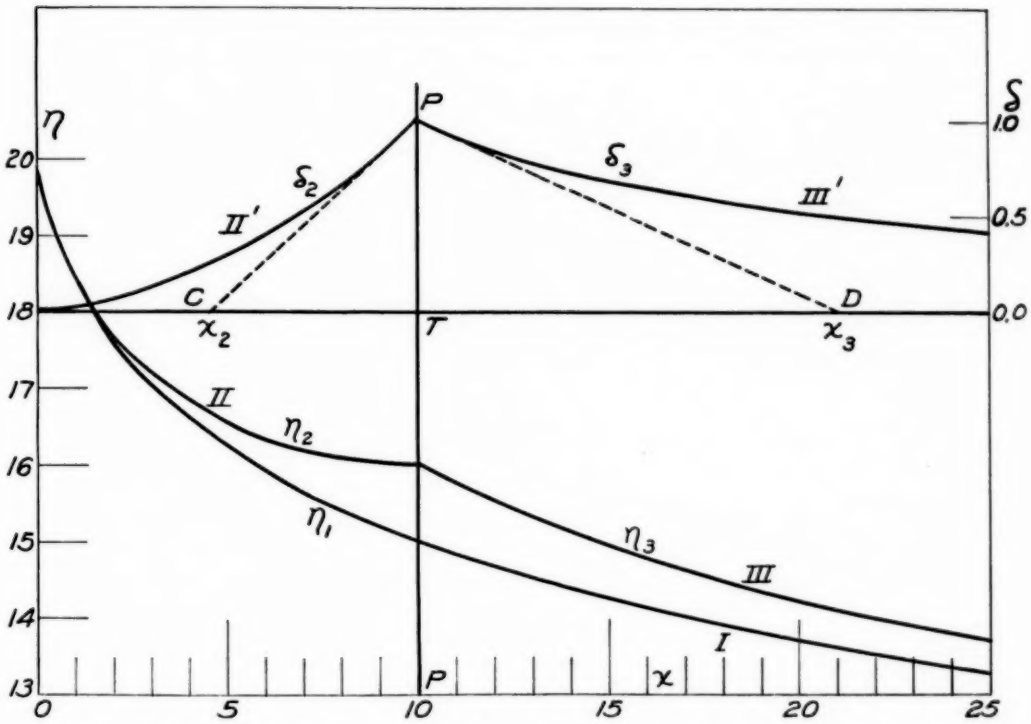

FIG. 1. Curves illustrating the perturbations in potential produced by a surface charge in an electron atmosphere.

where the subscript P is used to indicate that the derivation is taken at x_P.

Let us now draw tangents to the curves II′ and III′ at the point P and continue these lines to their intersections C and D with the horizontal axis. Let x_2 and x_3 be the values of x at these points. Then we have

$$x_3-x_P=-\delta_P/(\partial\delta_3/\partial x)_P=(x_P+x_L). \quad (87)$$

Similarly from Eq. (85), if we neglect x_L^3 compared to $(x_P+x_L)^3$ we find

$$x_P-x_2=\delta_P/(\partial\delta_2/\partial x)_P=\tfrac{1}{2}(x_P+x_L). \quad (88)$$

If we do not neglect x_L in this calculation we obtain for $x_P=x_L$ a value 14/17 as great as that given above, while for the case that $x_P\ll x_L$ we find

$$x_2=(2/3)x_P^3x_L^{-2}. \quad (89)$$

The forces acting on the charges at P are thus the same as if the electron atmosphere which produces the field $\eta_1(x)$ were replaced by two conducting planes located at x_2 and x_3. The force experienced by each electron (or ion) at P may be regarded as due to the images of all the electrons in P produced by the planes at x_2 and x_3. The total force on all the electrons on the plane P varies in proportion to the square of their number or the force on each one varies in proportion to the surface charge density. This is due to the fact that each electron is acted on not only by its own image but by the images of its neighbors in the plane P.

If we had a single electron on plane P, or if the electrons on P were at distances apart large compared to x_P-x_2 or x_3-x_P, then the forces on each electron may be regarded as due to its images in two reflecting planes which are approximately at x_2 and x_3. An exact determination of positions of these reflecting planes for a single electron at P is a two-dimensional problem which will usually be beyond our mathematical resources. If we assume that the reflecting planes are at x_2 and x_3, we obtain for the force on a single electron

$$F=(e^2/4)[(x_3-x_P)^{-2}-(x_P-x_2)^{-2}] \quad (90)$$

or by Eqs. (87) and (88)

$$F=-(3/4)e^2(x_P+x_L)^{-2}. \quad (90a)$$

By thus assuming that the reflecting planes for point charges are the same as for a distribution of charges over a plane, we fail to consider the segregation that occurs close to the point charge because of the high field strengths near the point. The error will evidently be negligible if the concentration of displacable charges near the plane P is small compared to that near the planes at x_2 or x_3. Although Eqs. (90) and (90a) are not exact, it is felt that they constitute very useful approximations which will not often cause errors of a serious nature. In a later section, in the derivation of Eq. (114), we shall have occasion to derive a more nearly exact expression for the image force on an electron near the boundary of a uniform plasma and shall compare it with an equation derived in the manner used for Eq. (90). This will serve to illustrate the degree of accuracy to be expected from Eq. (90).

Comparison of Eq. (90a) with the ordinary image force $-(1/4)e^2x_P^{-2}$ shows that when $x_P \gg x_L$, the effect of the electrons or ions in the space charge sheath is to exert on each electron an image force three times as great as that normally given by the metallic surface. Because of the perturbations produced by an individual electron on the motions of neighboring electrons, the electron does not induce an image in the metal but induces two virtual images in the sheath.

We have seen, however, that the image force becomes appreciable as a factor in determining the distribution of changes in the sheath only at distances less than x_F, and the effects of the image force are important only at distances comparable with x_s. Table I, columns 2, 3, and 5 show that x_F and x_s are small compared to x_L. By Eq. (89) we find for $x_P = 0.1\, x_L$ that $x_2 = 0.007\, x_P$ and thus conclude that even in the image sheath the space charge effects we have been considering are of no practical importance in modifying the image force. The principles involved in these calculations, however, will be useful in considering conditions very near the surface within the image sheath where the concentration gradients of the electron atmosphere reach enormous values.

Free path of perturbations

According to the Debye-Hückel theory, a disturbance in potential in a plasma produces perturbations which decrease with the distance in proportion to $\exp(-r/\lambda)$ where λ is given by Eq. (2). By analogy with the free paths of molecules in a gas we may thus regard λ as the mean free path of perturbations in a plasma or $1/\lambda$ is the absorption coefficient of plasma perturbations.

Let us consider, for example, the effect of placing a small uniform surface charge on a plane surface P within an infinite plasma. The potential at P is thus raised by an amount δ_P but elsewhere at a distance x from the plane the potential is

$$\delta = \delta_P \exp(-x/\lambda). \tag{91}$$

The potential gradient close to P ($x=0$) which is δ_P/λ is the same as though the plasma were replaced by two conducting surfaces one on each side of P and at the distance λ from it. We may thus consider that each electron in the plane P is acted on by two image forces of magnitude $e^2/4\lambda^2$ which act in opposite directions and thus balance. The distance λ may also be regarded as the distance at which δ has fallen to $1/\epsilon$th value.

In the space charge sheath where there are large concentration gradients we have seen that potential perturbations gradually decrease (see Fig. 1) as the distance from the disturbance increases and that this rate of decrease is greater in regions of high concentration. We may inquire whether in such cases it is useful to consider that there is an *absorption* of the perturbations corresponding to a definite free path.

In presence of a concentration gradient the free path λ_F can no longer be identified with λ as given by Eq. (2). We may consider, however, that the absorption coefficient is equal to $1/\lambda$ where

$$\lambda = (kT/4\pi e^2 n)^{1/2} = 9.792\,(T/n)^{1/2}\ \text{cm}^{-1} \tag{92}$$

and then as before may define the free path λ_F as the distance at which δ/δ_P is $1/\epsilon$. When λ varies with x, Eq. (91) is not applicable but instead we have

$$d \ln \delta/dx = -1/\lambda. \tag{93}$$

Integration gives $\ln(\delta/\delta_P) = -\int_{x_P}^{x} (1/\lambda)dx.$

Putting $\delta/\delta_F = 1/\epsilon$ and $x = x_3$ or x_2 in accord with Fig. 1 we obtain

$$\int_P^{x_3} \lambda^{-1} dx = 1 \quad \text{or} \quad \int_{x_2}^{x_P} \lambda^{-1} dx = 1 \qquad (94)$$

and the free path λ_F is then $\lambda_F = x_3 - x_P$ or $\lambda_F = x_P - x_2$.

Let us now apply this method to calculate λ_F within the space charge sheath and compare the results with those given by Eqs. (87) and (88). From Eqs. (92) and (32)

$$\lambda = 2^{-1/2}(x + x_L). \qquad (95)$$

Substituting this in Eqs. (94), we find

$$\left.\begin{aligned} x_3 - x_P &= [\exp(2^{-1/2}) - 1](x_P + x_L) \\ \text{and} \\ x_P - x_2 &= [1 - \exp(-2^{-1/2})](x_P + x_L) \end{aligned}\right\} \qquad (96)$$

or combining with Eq. (95) and introducing the numerical value of $\exp(2^{-1/2}) = 2.0281$,

$$x_3 - x_P = 1.0281\,(2)^{1/2}\,\lambda_P \quad \text{and}$$
$$x_P - x_2 = 1.0139\,(2)^{-1/2}\,\lambda_P, \qquad (97)$$

while Eqs. (87) and (88) give

$$x_3 - x_P = 2^{1/2}\,\lambda_P \quad \text{and} \quad x_P - x_2 = 2^{-1/2}\,\lambda_P. \qquad (98)$$

Thus, although the method of calculating the location of the reflecting planes involving the concept of perturbation free path does not give a result identical with that of the "exact" method, the errors resulting when it is applied to the space charge sheath are relatively small (less than 3 percent).

The free path method, although only approximate, is useful because of its wide applicability even in cases where mathematical difficulties prevent the use of the exact method. There are some cases, however, where the concentration varies with x in a discontinuous manner, in which the free path method may fail more or less completely as illustrated by the example in the following section.

The concept of perturbation free path λ may often be applied usefully to electron or ion distributions which are not of the Maxwellian type. Thus we may interpret Eq. (92) as indicating that in general λ varies inversely as the square root of the concentration of perturbable particles and in proportion to the square root of their average kinetic energy L so that

$$\lambda = (L/6\pi e^2 n)^{1/2} \qquad (99)$$

may be applied at least approximately to non-Maxwellian distributions.

IV. Image Forces Near the Boundary of a Plasma

Potential distribution

If we consider a semi-infinite region (bounded by a plane surface S, see Fig. 2) which contains both electrons and ions in thermal equilibrium at temperature T, we obtain in place of Eq. (80) the following equation for the potential distribution

$$d^2\eta/dx^2 = (\sinh \eta)/x_0^2, \qquad (100)$$

where in accord with Eq. (2)

$$\lambda_0 = (kT/8\pi e^2 n_0)^{1/2}. \qquad (101)$$

In the case of a typical plasma in which the concentrations of electrons and ions are nearly equal, the deviations δ from the normal plasma

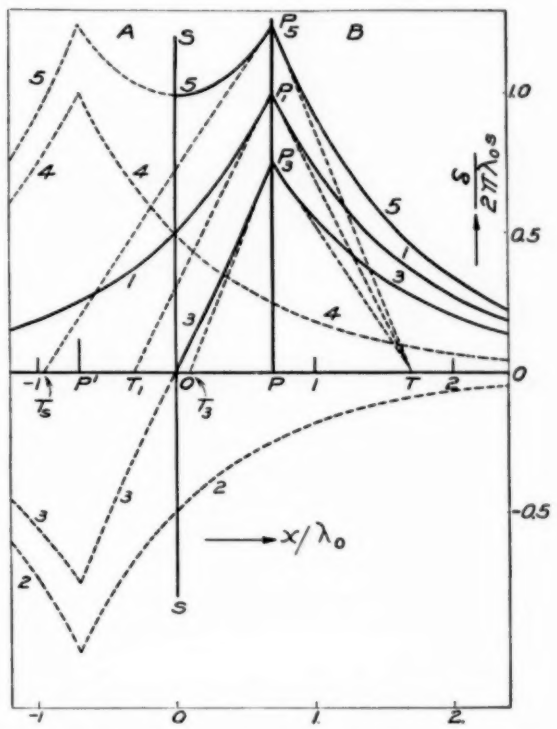

FIG. 2. Potential distributions produced by a surface charge in a plasma near the plasma boundary.

potential ($\eta=0$) are small so that Eq. (100) becomes

$$\lambda_0^2 d^2\delta/dx^2=\delta. \tag{102}$$

Integration gives

$$\lambda_0^2(d\delta/dx)^2=\delta^2+A, \tag{103}$$

where A is an integration constant.

If $d\delta/dx=0$ for $\delta=0$, $A=0$ and a second integration gives

$$\delta=\delta_0 \exp(\pm x/\lambda_0). \tag{104}$$

This is the case already considered by Debye and Hückel which led to Eq. (91). It corresponds to the case where a disturbing charge is located at an infinite distance from the plasma boundary.

The curve 1 in Fig. 2 illustrates the potential distribution as given by Eq. (104) when a surface charge, or uniform surface density s, is placed on a plane surface P. The two branches of the curve which meet at P_1 correspond to different values of the integration constant δ_0. The slopes of the curve at P_1, being related to the surface charge density s, enable us to eliminate δ_0 and we so obtain.

$$\delta=2\pi\lambda_0 s \exp(-\xi/\lambda_0), \tag{105}$$

where

$$\xi=|x-x_P|. \tag{106}$$

Boundary conditions

When $A\neq 0$ we have two integration constants to determine from the conditions existing at the plasma boundary.

To make our treatment more general let us consider that the plane S is the boundary between two plasmas A and B for which the values of n_0 are different. For example, B may be taken to be a gaseous plasma containing ions and electrons with moderate concentrations, while A may be a metal which, because of the free electrons and ions contained in it, may for the present purposes be regarded as a plasma of extremely high concentration. On the other hand, we may also take a case in which the concentration in A is zero as it would be, for example, if we take B to be a gaseous plasma bounded at S by a nonconducting surface such as a glass wall.

We shall reserve for a later section (Part 2) a consideration of the conditions at S which enable the two plasmas to be in equilibrium. For the present we need only point out that we shall have two limiting cases to consider when $n_A \gg n_B$ and when $n_A \ll n_B$. We wish in both cases to consider the forces which act on a charge at P in plasma B located near the boundary S.

The electric field surrounding the charge at P dies away at greater distances by a kind of absorption. The residual field which reaches as far as S acts to cause a displacement of the electron and ion atmospheres with respect to one another which results in a surface charge on S. For example, if the ion and electron concentration in A is very large compared to that in B, a negative charge at P tends to induce a positive charge on S which, in the limiting case, will prevent the field from extending an appreciable distance into A and make S an equipotential surface corresponding to $\delta=0$ (Case I).

On the other hand (Case II), with $n_A \ll n_B$, there is a tendency for a negative charge at P to displace the electrons near S out into A, which is equivalent to inducing a *negative* charge in the surface S. In the limiting case this may go so far as to neutralize the field at S originating from P so that as a boundary condition at S we have $d\delta/dx=0$.

Case I. $n_A \gg n_B$; $\delta=0$. Since in this case the value of $d\delta/dx$ at $\delta=0$ cannot be imaginary, we see by Eq. (103) that $A>0$. Integration then gives the result that between 0 and P, δ varies in proportion to $\sinh(x/\lambda_0)$ as shown by the full line $0P_3$ in Fig. 2. In plasma A there will be no appreciable potential gradient; the resulting discontinuity in the slope of the potential curve indicates that the effect of the charge at P is to induce a surface charge of opposite sign at S.

The potential distribution in plasma B is evidently the same as if, instead of considering a boundary at S, we assume the concentration in A is the same as in B, but assume also that there exists at P' a surface charge of density $-s$. From symmetry we see that the condition $\delta=0$ at $x=0$ is then fulfilled. The potential distribution as shown by curve 3 in Fig. 2 is thus obtained by adding the potential given by curve 1 to that of the image P' as given by curve 2. Thus from Eq. (105) we have for the whole of curve 3,

$$\delta_3=2\pi\lambda_0 s[\exp(-\xi/\lambda_0)-\exp(-\xi'/\lambda_0)], \tag{107}$$

where ξ and ξ' are the absolute values of the distances from P and P'. Between 0 and P, i.e., for $x<x_P$, after applying Eq. (106), this becomes

$$\delta_3=4\pi\lambda_0 s\exp(-x_P/\lambda_0)\sinh(x/\lambda_0), \quad (108)$$

while beyond P, for $x>x_P$, we have

$$\delta_3=4\pi\lambda_0 s\exp(-x/\lambda_0)\sinh(x_P/\lambda_0). \quad (109)$$

Curve 3 in Fig. 2 was calculated from these equations for the case that $x_P/\lambda_0=0.7$.

Image forces

If we draw tangents to curves 1 and 3 at the points P_1 and P_3, as indicated by the dotted lines, and determine their intersections T, T_1, and T_3 with the horizontal axes in accord with Eqs. (87) and (88), we obtain the locations of the "reflecting planes." Thus letting x_T, x_1 and x_3 be the abscissas at T, T_1 and T_3, we have

$$x_T-x_P=x_P-x_1=\lambda_0 \quad (110)$$

and

$$x_P-x_3=\lambda_0\tanh(x_P/\lambda_0). \quad (111)$$

In accord with Eq. (86) we may now calculate the force or pressure p exerted by these fields on the charges at the plane P. For Case I corresponding to P_3 we find

$$P_3=-2\pi s^2\exp(-2x_P/\lambda_0). \quad (112)$$

We may now calculate by Eqs. (90), (110) and (111) the force that would act on a single electron located in the plane P (in the absence of a uniform charge on P).

$$F_3=-(e/2\lambda_0)^2\operatorname{csch}^2(x_P/\lambda_0). \quad (113)$$

It should be noted that this equation was derived by the same method that was used for Eq. (90) *viz.*, by assuming that the reflecting plane for a point charge is the same as that for charges uniformly distributed on a plane.

In the present case with a uniform plasma we do not need, however, to make this simplifying assumption. In fact, in Eq. (60) we already have an exact solution of the problem of the force on an electron near the boundary of a plasma (exact, if we can assume the validity of Eq. (102)). This equation may be written

$$F=-(e/2\lambda_0)^2\epsilon^{-2\theta}(1+2\theta)/\theta^2, \quad (114)$$

where

$$\theta=x_P/\lambda_0. \quad (115)$$

Substituting Eq. (115) in Eq. (113), expanding in powers of θ and comparing with a similar expansion of Eq. (114), we have

$$F_3=-(e/2\lambda_0)^2(1/\theta^2)\times[1-(1/3)\theta^2+(1/15)\theta^4\cdots] \quad (116)$$

and

$$F=-(e/2\lambda_0)^2(1/\theta^2)\times[1-2\theta^2+(8/3)\theta^3\cdots]. \quad (117)$$

For large values of θ we can put in Eq. (113) $\operatorname{csch}\theta=2\exp(-\theta)$ and thus from Eq. (114) find that

$$F/F_3=(1+2\theta)/4\theta^2. \quad (118)$$

These equations enable us to estimate the magnitude of the errors introduced by the assumption, used in deriving Eq. (90), that the location of the reflecting plane for point charges is the same as for charges distributed over a plane. Serious errors are likely to occur only when a large fraction of the lines of force emanating from an electron fail to reach the reflecting plane S because of segregation in plasma B.

Case II. $n_A\ll n_B$; $d\delta/dx=0$. This condition is the same as if we replace the plasma A by one having the same concentration as B, but assume that at P' there exists a surface charge of density $+s$. The potential distribution as illustrated by curve 5 is obtained by adding the potentials as given by curve 1 and its image (curve 4). By Eq. (105) we thus have for curve 5

$$\delta_5=2\pi\lambda_0 s[\exp(-\xi/\lambda_0)+\exp(-\xi'/\lambda_0)]. \quad (119)$$

Between 0 and P, for $x<x_P$, this gives

$$\delta_5=4\pi\lambda_0 s\exp(-x_P/\lambda_0)\cosh(x/\lambda_0) \quad (120)$$

and for $x>x_P$

$$\delta_5=4\pi\lambda_0 s\exp(-x/\lambda_0)\cosh(x_P/\lambda_0). \quad (121)$$

Proceeding as in the derivation of Eq. (111) we find

$$x_P-x_5=\lambda_0\coth(x_P/\lambda_0). \quad (122)$$

The pressure on the plane P calculated by Eq. (86) comes out to be the same as that given

by Eq. (112) except that the sign before the second member is reversed.

Using Eq. (90) to calculate the force F_δ on a single electron at P we obtain

$$F_\delta = +(e/2\lambda_0)^2 \operatorname{sech}^2 (x_P/\lambda_0), \qquad (123)$$

whereas by the method that led to Eq. (60), considering the repulsion between two charges of like sign, we again get Eqs. (114) and (117), but with their signs reversed. From Eq. (123) for small values of θ we have

$$F_\delta = +(e/2\lambda_0)^2[1-\theta^2+(2/3)\theta^4 \cdots]. \qquad (124)$$

Comparing this with Eq. (123) we see that F_δ and F do not agree at all for small values of θ. Of course, if $d\delta/dx$ is actually 0 at $x=0$, the value of $-F$ given by Eq. (123) should be correct. Eq. (124) corresponds more nearly to a case in which the surface charge at S is zero: a case which will usually be approximately fulfilled when an electron is near the boundary of a plasma. In Part II we shall find cases when both of these equations are applicable. A more definite knowledge is needed of the conditions which determine the equilibrium of the electrons and ions near the plasma boundary, before a proper choice of the equations can be made.

In any case, it is clear that when two plasmas having different concentrations are separated by a bounding surface, each charged particle near the boundary, but in the more dilute plasma, is acted on by an image force which tends to draw it towards the boundary. In the more concentrated plasma, however, the image force on a particle near the boundary tends to repel it from the boundary. Under equilibrium conditions these image forces are balanced by the potential gradients due to space charges and by the pressure gradients of the electron and ion atmospheres.

V. Electrons with a Fermi Distribution

Electron sheath inside the metal

For electron concentrations greater than 10^{21} at temperatures up to 1000° the electron gas is nearly completely degenerate. For this case Fermi[35] has shown that the distribution of electrons in a field of force is given by

$$n = (2^{9/2}\pi m^{3/2} e^{3/2}/3h^3)\, V^{3/2}, \qquad (125)$$

where V is the potential at any point. Expressing V in volts

$$n = 4.602\times 10^{21} V^{3/2} \text{ cm}^{-3}. \qquad (126)$$

At any point the kinetic energies of the electrons range from 0 up to V electron-volts, the average energy being $(3/5)V$.

Many of the features of a metal may be represented by a model consisting of a plasma containing an electron Fermi gas imbedded in a positive continuum of equivalent charge.

The distribution of potential and electron concentration in the plasma can now be obtained by combining Eq. (125) with Poisson's equation giving

$$\lambda_1^2(d^2\varphi/dx^2) = \tfrac{2}{3}(\varphi^{3/2}-1) \quad \text{for } x<0, \qquad (127)$$

where φ is a dimensionless variable proportional to V defined by

$$\varphi = V/V_1, \qquad (128)$$

where V_1 is the "inner potential" which is related to the electron concentration n_1 in the metal as follows,

$$V_1 = 2.452\times 10^{-4} n_1^{1/6}. \qquad (129)$$

This is obtained from Eq. (126) by putting $n=n_1$ and solving for V. The parameter λ_1 in Eq. (127) has the dimensions of a length and is

$$\lambda_1 = \frac{2^{1/4}}{8\pi}\,\frac{h^{3/2}}{e^{5/4}m^{3/4}V_1^{1/4}} = 0.898\times 10^{-8} V_1^{-1/4} \text{ cm} \qquad (130)$$

or if use is made of Eq. (125) λ_1 may be expressed in the simpler form

$$\lambda_1 = (1/4\pi)(\pi/3)^{1/6}(h/em^{1/2}n_1^{1/6}) = 3.662\times 10^{-5} n_1^{-1/6} \text{ cm}. \qquad (131)$$

In order to determine the perturbations in the plasma potential produced by a disturbing charge on a plane P which lies within the plasma parallel to the bounding surface S (see Fig. 1) we may put in Eq. (127) $\varphi = 1+\delta$, and so obtain

$$\lambda_1^2(d^2\delta/dx^2) = \delta. \qquad (132)$$

Since this is identical with Eq. (102), we may

[35] E. Fermi, Zeits. f. Physik **36**, 902 (1926), and ibid. **48**, 73 (1928).

apply Eqs. (108) to (113) without change to the present case. When the free path method is applicable, the parameter λ_1 as given by Eqs. (130) or (131) is thus the perturbation free path in a Fermi plasma.

Fermi sheath outside of a metal surface

The electron pressure in the metal must be balanced by forces acting on the electrons near the plasma boundary. These forces are of two kinds: electric forces due to the potential drop in a double sheath and image forces acting on the electrons within this sheath. Let us postpone the consideration of the image forces to a later section.

In accord with the model we have adopted we consider the surface of the metal to be the plane S which bounds the positive ion continuum. For $x<0$, Eq. (127) applies, but for $x>0$, since the positive charge is absent, the equation becomes

$$\lambda_1^2(d^2\varphi/dx^2)=\tfrac{2}{3}\varphi^{3/2}, \quad \text{for } x>0 \text{ and } \varphi>0. \quad (133)$$

We see from Eq. (125) that n falls to 0 at $V=0$ and therefore

$$d^2\varphi/dx^2=0 \quad \text{for } \varphi<0. \quad (134)$$

The potential distribution obtained by integrating these equations with various boundary conditions are shown in Fig. 3.

We shall wish to consider the conditions at the surface when an approaching electron exerts a large force on the electrons in the sheath. This external field may be taken into account by considering that for $\varphi<0$, $dv/dx=E$ or

$$\lambda_1(d\varphi/dx)=E\lambda_1/V_1\equiv-\beta \quad \text{for } \varphi<0, \quad (135)$$

where β is a dimensionless parameter.

The curves in Fig. 3 were calculated for $\beta=0$ and for various positive values of β corresponding to external retarding fields acting on electrons leaving the metal.

We may now integrate Eqs. (127) and (133) subject to the conditions $d\varphi/dx=0$ at $\varphi=1$ and $\lambda_1 d\varphi/dx=\beta$ at $\varphi=0$ and so obtain

$$\lambda_1^2(d\varphi/dx)^2=(8/15)\varphi^{5/2}-(4/3)\varphi+4/5 \quad \text{for } x<0 \quad (136)$$

and

$$\lambda_1^2(d\varphi/dx)^2=(8/15)\varphi^{5/2}+\beta^2 \quad \text{for } x>0 \text{ and } \varphi>0. \quad (137)$$

At $x=0$ the values of $d\varphi/dx$ given by these two equations must be equal. Let φ_S be the value

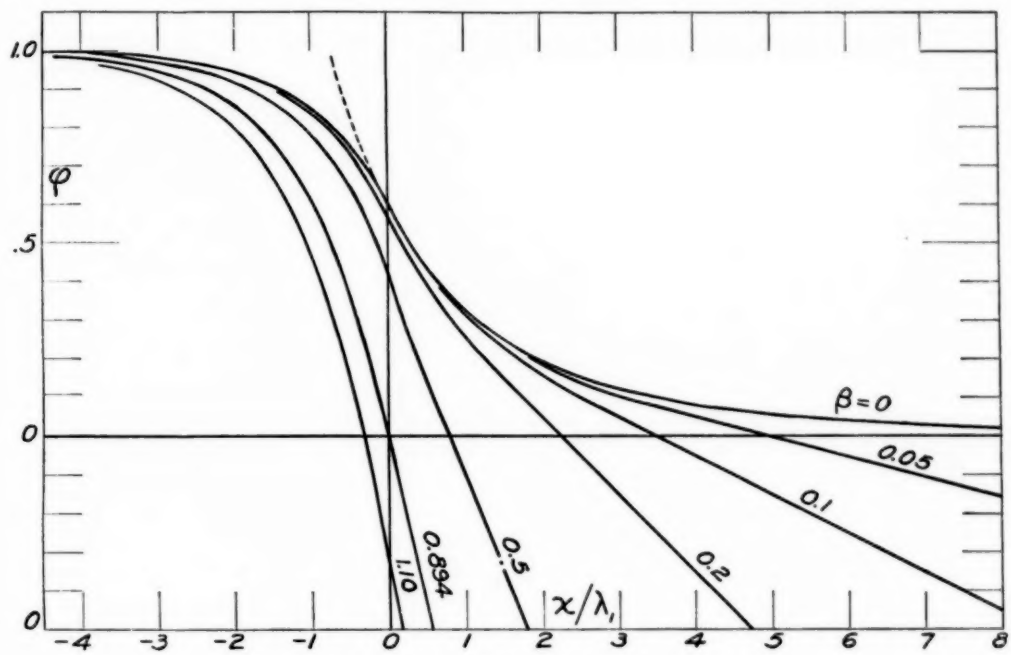

FIG. 3. Potential distribution in the Fermi sheath.

of φ at the bounding surface $S(x=0)$, then

$$\varphi_S = 3/5 - (3/4)\beta^2. \quad (138)$$

Within the metal for $x<0$, we put $\varphi = 1+\delta$ in Eq. (136), expand in powers of δ, and integrate, determining the integration constant by the condition $\delta = \delta_s = \varphi_s - 1$ at $x=0$ and so obtain

$$x/\lambda_1 = \ln(\delta/\delta_s) - (1/12)(\delta - \delta_s) + (1/96)(\delta^2 - \delta_s^2). \quad (139)$$

This series converges sufficiently rapidly to give the potential distribution even when $\varphi_s = 0$ or $\delta_s = 1$.

For $x>0$ we must consider several cases.

Case I. $\beta = 0$. Integration of Eq. (137) with the boundary condition $\varphi = \varphi_s$ at $x=0$ gives

$$x/\lambda_1 = (30)^{1/2}\varphi^{-1/4} - 6.224 \quad (140)$$

or

$$\varphi = 900\lambda_1^4(x+6.224\lambda_1)^{-4} = 0.6(1+x/6.224\lambda_1)^{-4}. \quad (141)$$

By means of Eqs. (130) and (128) this may be expressed

$$V = 1800(8\pi)^{-4}h^6e^{-5}m^{-3}(x+6.224\lambda_1)^{-4} = 5.85\times10^{-26}(x+6.224\lambda_1)^{-4} \text{ volts}. \quad (142)$$

Thus when $\beta = 0$ the potential in the sheath of Fermi gas outside the metal varies inversely as the fourth power of the distance from a plane inside the metal located at $x = -6.224\lambda_1$. The constant factor is a universal constant. The electron concentration varies inversely as the sixth power of this distance. The data for the curves marked $\beta = 0$ in Fig. (3) were calculated by Eqs. (139) and (140).

Case II. $\beta^2 < 0.8$. When β has positive values, the curve giving $\varphi(x)$ crosses the X axis at some point x_0. Integration of Eq. (137) gives

$x_0/\lambda_1 = I_S$ where

$$I_S = \int_0^{\varphi_s} d\varphi[(8/15)\varphi^{5/2} + \beta^2]^{-1/2}. \quad (143)$$

Let us put

$$I_S = I_\infty - (I_\infty - I_S), \quad (144)$$

where I_∞, the definite integral obtained by putting ∞ in place of φ_s in Eq. (143), can be calculated in terms of gamma-functions and is found to have the value

$$I_\infty = 6.124\beta^{-1/5}. \quad (145)$$

Expanding the integrand of Eq. (143) in powers of $\beta^2\varphi_s^{-5/2}$ and integrating we get

$$I_\infty - I_S = 30^{1/2}\varphi_s^{-1/4} \times (1 - 0.0853\beta^2\varphi_s^{-2.5} + 0.062\beta^4\varphi_s^{-5}\cdots) \quad (146)$$

which converges rapidly when $\beta < 0.3$.

For small values of β, where by Eq. (138) $\varphi_S = 0.6$, Eq. (146) gives $I_\infty - I_S = 6.224$. For $\beta = 0.3$ this increases only about 2 percent. Thus by Eqs. (143), (144) and (145) for values of β up to 0.3 or 0.4 we have

$$x_0/\lambda_1 = 6.124\beta^{-1/5} - 6.224. \quad (147)$$

A different expansion of Eq. (137) gives

$$(x_0 - x)/\lambda_1 = (\varphi/\beta) \times [1 - (8/105)\beta^{-2}\varphi^{5/2} + (4/225)\beta^{-4}\varphi^5]. \quad (148)$$

When $\beta > 0.5$ this may be used for calculating x_0 by putting $x=0$ and $\varphi = \varphi_s$.

Case III. $\beta^2 > 0.8$. When β^2 reaches 0.8, Eq. (138) shows that φ_s becomes zero. For larger values of β the electron concentration falls to zero at some point within the metal, that is, $x_0 < 0$.

For $x < x_0$ the potential distribution is obtained from Eq. (139) by putting $\delta_s = 1$ and replacing x by $x - x_0$.

The effect of these strong fields is to displace the electron distribution without changing the shape of the curve $\varphi(x)$. At x_0 the potential gradient is given by

$$\lambda_1(d\varphi/dx)_0 = -(0.8)^{1/2} = -0.894, \quad (149)$$

which is the same as that outside the metal when $\beta = 0.894$ and $\varphi_s = 0$.

When $\beta^2 > 0.8$ there are no electrons between $x = x_0$ and $x = 0$ so that Eq. (127) reduces to

$$\lambda_1^2(d^2\varphi/dx^2) = -2/3. \quad (150)$$

At $x=0$ we must have $\lambda_1 d\varphi/dx = -\beta$ and at x_0, $\varphi = 0$. Integration thus gives

$$\varphi = -\beta(x - x_0)/\lambda_1 - \tfrac{1}{3}(x^2 - x_0^2)/\lambda_1^2 \quad \text{for } x_0 < x < 0. \quad (151)$$

Solving Eqs. (149) and (151) for x_0 we find that the displacement of the electrons is given by

$$x_0/\lambda_1=(3/2)(0.894-\beta). \tag{152}$$

Substituting this in Eq. (151), placing $x=0$, and comparing with Eq. (138) we find that this equation is still applicable when $\beta^2>0.8$.

Perturbations and image forces within the Fermi sheath

Putting $\varphi=\varphi_1+\delta$ in Eq. (133), the perturbations in the Fermi sheath outside the metal are seen to be governed by the equation

$$\lambda_1^2(d^2\delta/dx^2)=\varphi_1^{1/2}\delta, \tag{153}$$

where φ_1 is a function of x which represents the potential distribution in the undisturbed state as obtained by the solution of Eq. (133). In general Eq. (153) cannot be readily integrated.

Case I. $\beta=0$. For this case by substituting the value of φ_1 from Eq. (141) into Eq. (153) and integrating we find

$$\delta=A(x+6.22\lambda_1)^6+B(x+6.22\lambda_1)^{-5}. \tag{154}$$

This may be handled in the same manner as Eq. (83). If the point P (see Fig. 1) is sufficiently far from the surface S so that δ_2 has fallen practically to zero at S, then in place of Eqs. (85) and (84) we find

$$\delta_2=A(x+6.22\lambda_1)^6; \qquad \delta_2=B(x+6.22\lambda_1)^{-5} \tag{155}$$

and the positions of the reflecting planes (cf. Eqs. (87) and (88)) are given by

$$\left.\begin{aligned} x_3-x_P&=(1/5)(x_P+6.22\lambda_1),\\ x_P-x_2&=(1/6)(x_P+6.22\lambda_1).\end{aligned}\right\} \tag{156}$$

Thus by Eq. (90) the image force acting on the electrons is

$$F=-(11/4)e^2(x_P+6.22\lambda_1)^{-2}. \tag{157}$$

Let us compare these results with those given by the *free path method*. We have seen that for a uniform initial concentration the free path λ_1 is given by Eq. (130). For the non-uniform distribution in the sheath we may thus put

$$\lambda=\lambda_1\varphi_1^{-1/4}, \tag{158}$$

where φ_1 is given by Eq. (141). We thus find for the Fermi sheath

$$\lambda=(30)^{-1/2}(x+6.22\lambda_1). \tag{159}$$

This differs from the expression obtained for the space charge sheath, Eq. (95), only in the value of the two constants. Let us therefore generalize Eq. (159) by putting

$$\lambda=[\alpha(\alpha-1)]^{-1/2}(x+a), \tag{160}$$

so that Eqs. (95) and (159) are now special cases corresponding to $\alpha=2$ and $\alpha=6$, respectively. Introducing this value of λ in Eq. (94), we find

$$(x_P+a)/(x_3+a)=(x_2+a)/(x_P+a)=\exp\{-[\alpha(\alpha-1)]^{-1/2}\}=1-1/\alpha-1/24\alpha^3-1/48\alpha^4. \tag{161}$$

To compare this with the result of the exact method, let us see what potential distribution $\varphi_1(x)$ corresponds to the generalized Eq. (160). Eliminating λ from Eqs. (158) and (159) we have

$$\varphi_1=[\alpha(\alpha-1)]^2\lambda_1^4(x+a)^{-4} \tag{162}$$

instead of Eq. (141). Substituting this in Eq. (153) and integrating as before, we now find in place of Eq. (155)

$$\delta_2=A(x+a)^\alpha \quad \text{and} \quad \delta_3=B(x+a)^{-(\alpha-1)}. \tag{163}$$

The method of Eqs. (87) and (88) then gives in place of Eq. (161)

$$(x_P+a)/(x_3+a)=(x_2+a)/(x_P+a)=1-1/\alpha. \tag{164}$$

Comparing this with Eq. (161) we conclude that the free path method and the exact method agree whenever we can neglect $(1/24)\alpha^3$ compared to unity. For the case we are considering where $\alpha=6$ this term is only 0.00019. We find from Eq. (161) that in this case the free path method gives values of x_3-x_P and x_P-x_2, which are greater than those of Eq. (156) by only 0.15 percent and 0.13 percent, respectively.

Case II. $\beta^2<0.8$. Since for $x>x_0$ there is no space charge, the potential distribution is represented by the straight line

$$\lambda_1\varphi=-\beta(x-x_0). \tag{165}$$

Consider now that at some plane P for which $x_P>x_0$ we raise the potential corresponding to

an amount $\delta\varphi$. This changes β by $\delta\beta$ and x_0 by δx_0 so that we have

$$\lambda_1\delta\varphi=\beta\delta x_0-(x-x_0)\delta\beta. \tag{166}$$

By the method used in Eq. (88) we then obtain

$$x_0-x_2=-\beta(dx_0/d\beta). \tag{167}$$

By Eq. (147) this becomes

$$x_0-x_2=1.225\beta^{-1/5}\lambda_1=(1/5)(x_0+6.22\lambda_1). \tag{168}$$

For small values of β the potential distribution is still approximately a linear function of x for values of x considerably less than x_0. Thus we may apply the *free path method* by substituting the value of φ from Eq. (165) into (158) and the resulting value of λ into Eq. (94). This gives

$$x_0-x_2=1.195\beta^{-1/5}\lambda_1, \tag{169}$$

which is the same as Eq. (168) except that the constant is 2.5 percent smaller. This good agreement is of interest in view of the fact that the distribution of concentration has a discontinuity at x_0.

Case III. $\beta^2>0.8$. At $x=0$, $\varphi=\varphi_s$ as given by Eq. (138). For $x>0$, φ is a linear function of x so that

$$\varphi=\varphi_s-\beta x/\lambda_1=0.6-\beta x/\lambda_1-0.75\beta^2$$

and $\delta\varphi=-(1.5\beta+x/\lambda_1)\delta\beta$. By the method of Eq. (88), using also Eq. (151), we find

$$x_2=-1.5\beta\lambda_1=x_0-1.34\lambda_1. \tag{170}$$

The perturbation method thus locates the reflecting plane at a distance $1.34\lambda_1$ inside of the edge of the displaced Fermi electron gas. The total field $d\varphi/dx$ decreases linearly with x between $x=0$ and $x=x_0$, but the perturbations continue on through this region of constant positive space charge until they reach displaceable electrons. The potential distribution in this region (values of x slightly less than x_0) is approximately linear (see Fig. 3) and is given by Eq. (165) if β is put equal to 0.894, the value of $\lambda_1 d\varphi/dx$ at x_0. The value of x_0-x_2 given by the free path method is thus obtained by putting $\beta=0.894$ in Eq. (169) yielding $x_0-x_2=1.23\lambda_1$ which is in rough agreement with Eq. (170).

Effect of image force within the Fermi sheath

In calculating the electron distribution in the Fermi sheath by means of the Poisson equation and the Fermi equation, we have in effect assumed that the pressure gradient in the Fermi electron gas balances at every point the electric force due to the potential gradient resulting from the space charge. The problem we have solved is the one-dimensional analogue of the three-dimensional problem treated by Fermi in his study of the distribution of electrons in atoms.

In both of these treatments, however, the image forces acting on the electrons in the Fermi gas have been neglected. Let us consider the relative magnitudes of the image force and the electric force.

For the case that $\beta=0$ we find by putting $\varphi_s=0.6$ in Eq. (137) that the potential gradient at $x=0$ is

$$(dV/dx_0)=0.386V_1/\lambda_1. \tag{171}$$

The image force on an electron at $x=0$ can be obtained from Eq. (90) by putting $x_P=0$. The value of x_3 according to Eq. (156) is $x_3=1.245\lambda_1$. The value of $-x_2=1.039$ given by Eq. (156) is evidently too small for the electron concentration for $x<0$ is less than was assumed in the derivation of this equation. Using Eq. (139) for the distribution for $x<0$ and applying Eqs. (158) and (94) we find by the free path method $x_2=-1.072$. The image force is thus

$$F=0.0560e^2/\lambda_1^2.$$

Comparing this with Eq. (171) we find that the ratio of the image force to the force produced by the potential gradient is (see also Eq. (130)) $Fi/F_e=0.1453e/V_1\lambda_1=2.31V_1^{-3/4}$, where V_1 is in volts. Since V_1 has values that range from 1.5 for caesium to about 19 for tungsten, it appears that the image force in the sheath is by no means negligible but is often greater than the electric force.

The effects of this image force will resemble in many ways that produced by an external field corresponding to values of β comparable with unity (Fig. 3). Thus it compresses the Fermi sheath and gives it a definite outer edge at x_0, for the image force which extends far outside of x_0 prevents any of the Fermi electrons from going more than a definite distance. The electrons in the metal having components of kinetic energy normal to the surface equal to V_1 can thus pass freely to x_0. The work needed to remove electrons from

the metal (Richardson work function at $T=0$) is thus *the work that must be done against the image force in the region outside of* x_0 or is thus equal to the image motive at x_0. The image force within the sheath ($x<x_0$) is thus of importance only insofar as it is a factor determining the value of x_0 and the magnitude of the image force outside of x_0. The reason that the work done against the image force in removing an electron from the interior of the metal to x_0 is not included in the "work function" is that this force is balanced in this region by the electron pressure and the force due to the potential gradient.

In Part II a method will be developed for calculating the image forces on electrons which lie within the Fermi sheath even when the perturbations produced by an individual electron cannot be considered to be small. This theory will be applied to the forces which hold adsorbed caesium atoms on tungsten surfaces.

On the Mass Defect of Helium

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If one assumes that the potential energy between protons and neutrons has the shape of a simple potential hole, it is possible from the experimental value of the mass defect of the H^2, to derive a connection between the mean width and the depth of this curve. This connection proves to be, to a large extent, independent of the finer details of the potential curve. By assuming a certain probable value, obtained from scattering experiments, for the width of the potential hole, it is possible to make calculations on the mass defects of other nuclei. Such computations were carried out for He and yield values which are greater than the mass defect of H^2 by a rather large factor. This agrees with experiment. For the higher elements, the Pauli principle has to be taken into account and the structure of higher nuclei is discussed on this basis.

I.

THE discovery of the neutron by Chadwick,[1] and by Curie and Joliot[2] has made possible a more detailed picture of the constitution of the nuclei. As far as can be seen at present, there are three different assumptions possible concerning the elementary particles.

(a) The only elementary particles are the proton and the electron. This point of view has been emphasized by Heisenberg and treated by him in a series of papers.[3]

(b) The neutrons are elementary particles and the nuclei are built up by protons, electrons and neutrons. This point of view was proposed by Dirac and adopted by Bartlett[4] in his discussion of the constituents of the light elements.

(c) It may be assumed furthermore that in addition to the neutrons, discovered by Chadwick ("heavy neutrons") there are "light neutrons" of electronic mass, as first proposed by Pauli.[5] The number of light neutrons should be equal to the number of electrons in every nucleus and they leave the nucleus simultaneously with the β-rays. The number of electrons (and light neutrons) should be, just as in (b), equal to the number of "free electrons," as proposed by Beck.[6] Some arguments in favor of this assumption were given by the present author.[7]

For the present purpose (the comparison of the mass-defects of the first few elements) it does not make any difference whether we adopt the hypothesis contained in (b) or (c), because the first elements, even up to Cl, do not contain any free electrons. The calculations will probably hold, even if the hypothesis (a) is adopted.

There seem to be three alternative possible assumptions concerning the nature of the forces acting between protons and neutrons. (The forces between two protons or between two neutrons are always neglected.) Heisenberg assumed that these forces are of the exchange type, similar to those of the H_2^+ molecule. If we suppose, however, that the neutrons have to be treated as elementary particles, one must either assume a certain potential energy $V(r)$ between a proton and a neutron, or a three-body force. The present calculations will be made on the basis of the former assumption. The other possibility is to calculate with a potential energy which is a function of the mutual distance of *three* particles. Forces of this kind[8] must be assumed in the hypothesis (c) for

[1] Chadwick, Nature **129**, 469 (1932).

[2] Curie and Joliot, Comptes Rendus **193**, 1412 and 1415 (1931).

[3] W. Heisenberg, Zeits. f. Physik **77**, 1 (1932); **78**, 156 (1932).

[4] Cf. W. Bartlett, Phys. Rev. **42**, 145 (1932), (Letter to the Editor).

[5] Cf. Carlson and Oppenheimer, Phys. Rev. **38**, 1787 (1931).

[6] G. Beck, Zeits. f. Physik **47**, 407 (1928); **50**, 548 (1928).

[7] E. Wigner, Proc. Hung. Acad., 1932.

[8] An example for such a potential is $cE^2(1+e^{r/\rho})^{-1}$, where c is a constant, r the distance of the neutron from one proton and E the electric field strength produced by the other protons.

the light neutrons, so it does not seem unnatural to allow them for the heavy neutrons as well.

The effect of the first kind of forces was fully discussed by Heisenberg and the discussion of the effect of the forces of the second kind can be carried out in a very similar way. One interesting feature of the second kind of forces is that it is probable that if a nucleus with n_p protons and n_h neutrons is stable and if n_p is odd then there is also a stable nucleus with n_p+1 protons and n_h neutrons. Also if n_h is odd there probably exists a stable nucleus with n_p protons and n_h+1 neutrons. The reason for this is that if n_p is odd, the next proton may have the same wave-function as this one, which is in conflict with the Pauli principle if n_p is even. From O up to Cl the nuclei predicted in this way are all known. Below oxygen, however, there are some nuclei lacking, namely those with the (n_p, n_h) values (1, 2), (2, 1), (4, 3), (4, 6), (6, 5), (6, 8), (8, 7). A possible reason that these nuclei have so far escaped detection, together with a more exact proof of the above-mentioned rule, will be given in Section III, a different explanation of their constitution was put forward by Jones.[9]

It may be seen furthermore, that just as in the theory of Heisenberg, the energies of the nuclei (n, n') and (n', n) are equal. Consequently among all nuclei with the same mass $n+n'$ that with the charge $n_p=(n_p+n_h)/2$ will be the most stable, having the largest number $(n_p+n_h)^2/4$ of attracting terms. The formation of the nuclei after O^{16} may be imagined like this[4]: Assuming that the addition of a heavy neutron to O^{16} is connected with an energy gain, we get O^{17}. Then according to the preceding rule, the capture of another neutron is possible, giving O^{18}. By this process the number of neutrons is increased so much in the nucleus, that it may capture a new proton giving F and then another, giving Ne^{20}. Now by the increased number of protons the capture of a new neutron is possible, giving Ne^{21}, and with another one Ne^{22}, and so on.

In addition to the difficulty connected with the apparent non-existence of the above-mentioned nuclei, it seems rather surprising that the nuclei between O and Cl adhere so very closely to the condition $n_p=n_h$. This difficulty can be avoided, of course, by assuming a repulsive force between the neutrons and between the protons at small distances.

The potential, as suggested in reference eight is also capable of explaining the qualitative features of the series of existing elements in some respects even better than that just discussed. It does not seem, however, to be easy to make simple assumptions as to the general shape of such a potential.

II.

One of the remarkable facts about the mass defects in the very first elements is the very great binding energy of the He nucleus. The binding energy of the H^2 nucleus is only[10] three times the rest energy mc^2 of the electron, the binding energy of the He is[11] $52mc^2$, if we assume the mass of the neutron equal to the mass of the proton 1.00724 (referred to the mass of neutral O^{16}). The masses of the H^2 and He nuclei are taken to be 2.01297 and 4.00108, respectively. The binding energy of He is around 17 times larger than that of H^2.

This would rather indicate an attraction between the neutrons or between the protons, which is very unlikely on the basis of the previous discussion. The purpose of the subsequent calculation is to see how far it is possible to explain the large mass defect of He without such an assumption, or even to reconcile it with the existence of some repulsive forces between the different neutrons and also the different protons.

First we consider the H^2 nucleus. There are several indications that the first energy value depends only on the rough shape of the potential curve. For the H^2 nucleus, therefore, the potential energy was assumed for the purpose of the calculation to be

$$V(r)=4v_0/(1+e^{r/\rho})(1+e^{-r/\rho}) \qquad (1)$$

in units of mc^2, where v_0 and ρ are constants. The Schrödinger equation becomes in this case

$$\left[-10\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V\right]\psi(xyz)=\epsilon\psi(xyz), \quad (2)$$

where x, y, z are the components of the distance between the two particles, and the energy and

[9] E. G. Jones, Nature **130**, 580 (1932).

[10] K. T. Bainbridge, Phys. Rev. **42**, 1 (1932). J. D. Hardy, E. F. Barker and D. U. Dennison, Phys. Rev. **42**, 279 (1932).

[11] F. W. Aston, Proc. Roy. Soc. **A115**, 502 (1927).

distance are always measured in units mc^2 and e^2/mc^2, respectively, and we have for convenience set $h^2mc^2/4\pi^2 M = 10$. The characteristic numbers and functions of (2) with the potential (1) are known from the work of Eckart.[12] The lowest energy level is

$$-\epsilon = 50/8\rho^2 + v_0 - (30/8\rho^2)(1+8v_0\rho^2/5)^{1/2}, \quad (3)$$

while the corresponding (unnormalized) characteristic function is

$$\psi = \frac{\rho}{r}\frac{e^{r/\rho}-1}{e^{r/\rho}+1}\frac{1}{(1+e^{r/\rho})^{\nu}(1+e^{-r/\rho})^{\nu}} \quad (4)$$

with $\nu = (-\epsilon\rho_2/10)^{1/2}$. The function $V(r)$ is graphically given in Fig. 1 (heavy line). The constants ρ and v_0 must be chosen such that $\epsilon = -3$ should give the observed binding energy of H^2. This gives an equation between v_0, the potential for $r=0$, and ρ, the mean thickness of the potential hole, which is given in Fig. 2 (heavy line). In order to have a better insight into the conditions governing the behavior of the characteristic values and characteristic function, the characteristic function (4) for $\rho = 0.22$, $v_0 = 140$ is given by the broken line in Fig. 1. One sees that it extends over a much wider region than $V(r)$ and in consequence the mean potential energy is much smaller than v_0. In Fig. 3, the mean negative potential energy $-P$, the mean kinetic energy K and the negative total energy $-\epsilon = 3$ are plotted against the parameter ρ for the case in which v_0 is taken from Fig. 2, yielding (by Eq. (3)) $\epsilon = -3$. For small values of ρ, the negative mean potential energy is much larger than $-\epsilon$, and is almost totally compensated by the kinetic energy. Thus the value of ϵ is very sensitive to small variations of v_0, because these latter increase the mean potential energy without affecting the kinetic.

In order to have a check on the relative independence of the (v_0, ρ) curve on the exact shape of the potential function, another two-parameter family ae^{-br} of such functions was taken (light line in Fig. 1) and the parameters $a = 1.4v_0$, $b = 0.63/\rho$ have been chosen in such a way that this new potential be as similar to (1) as possible. The lowest energy-value was calculated then by a simple variational method (taking $\psi = e^{-\beta r}$) and then a and b adjusted in such a way that the lowest energy value be again -3. The light line in Fig. 2 gives the relation obtained in this way between $v_0 = a/1.4$ and $\rho = 0.63/b$. It runs very near to the line obtained for the potential-function (1). A more exact calculation would show that it runs yet a little lower than shown in Fig. 2.

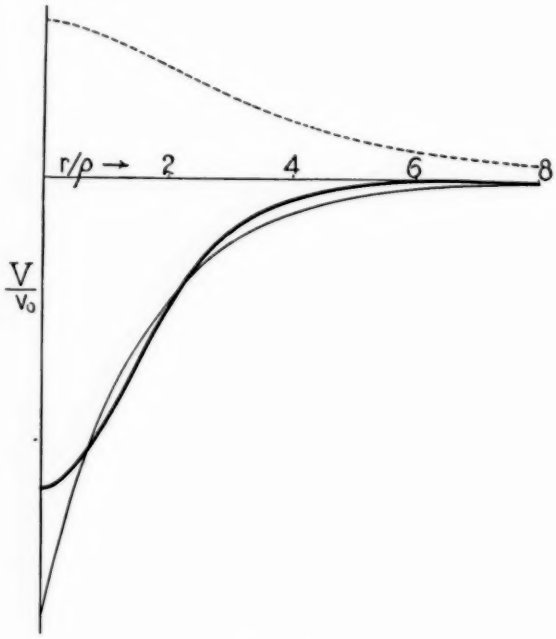

FIG. 1.

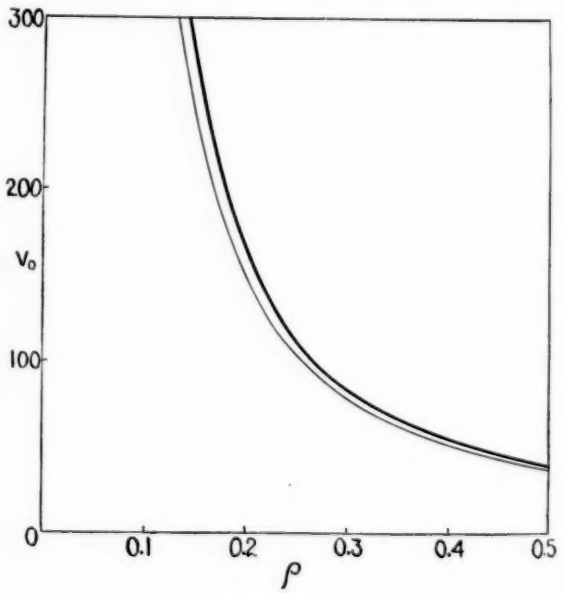

FIG. 2.

[12] C. Eckart, Phys. Rev. 35, 1303 (1930).

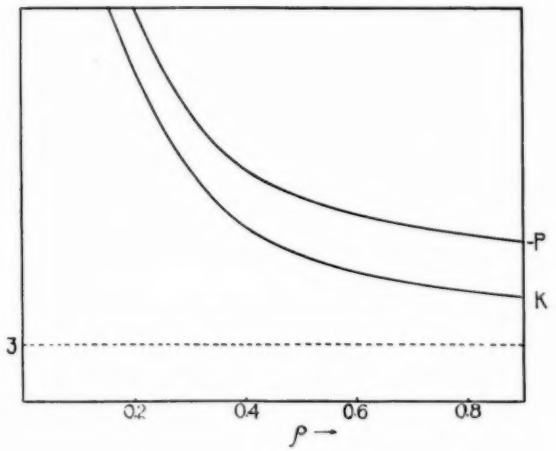

FIG. 3.

It is clear now what the cause of the large mass defect of He may be. The total energy of the He consists of four potential energies (the attraction of both protons on both neutrons) and only four kinetic energies, as contrasted to one potential energy and two kinetic energies in the H^2. In He therefore, the former will overcompensate the latter much more than in H^2. A similar phenomenon exists also in atomic spectra: the lowest energy value of the He is four times larger than that of H, because the ratio of the terms of potential to kinetic energy is 2 : 1 instead of 1 : 1 in H. The conditions are still more pronounced in the nucleus.

III.

Before making the actual calculation for He, a remark on the existence of H^3 should be added. The Schrödinger equation $H\psi = E\psi$ for two neutrons 1, 2 and a proton 3 is

$$-10\Big(\frac{\partial^2}{\partial r_{23}^2}+\frac{2}{r_{23}}\frac{\partial}{\partial r_{23}}+\frac{\partial^2}{\partial r_{13}^2}+\frac{2}{r_{13}}\frac{\partial}{\partial r_{13}}+\frac{\partial^2}{\partial r_{12}^2}+\frac{2}{r_{12}}\frac{\partial}{\partial r_{12}}+\cos(213)\frac{\partial^2}{\partial r_{12}\partial r_{13}}+\cos(123)\frac{\partial^2}{\partial r_{12}\partial r_{23}}$$
$$+\cos(132)\frac{\partial^2}{\partial r_{13}\partial r_{23}}\Big)\psi+(V(r_{13})+V(r_{23}))\psi=E\psi(r_{23},r_{13},r_{12}), \quad (5)$$

where (213) is the angle with the vertex 1 and the sides through 2 and 3. Assuming that $\psi(r_{13})$ is the solution of the Schrödinger Eq. (2) between the neutron 1 and the proton 3, it is reasonable to try the wave function

$$\psi_0=\psi(r_{13})\psi(r_{23}) \quad (6)$$

for (5). Actually, by calculating the expectation value for the energy $E_0=(\psi_0, H\psi_0)$ of ψ_0 we obtain -2ϵ. Therefore the binding energy of the second neutron is certainly even larger than that of the first.[13] This is independent of the potential function. The conditions will remain similar if we complete the odd number of protons or neutrons to an even number.

In order to have a better value for the mass defect of H^3 than -2ϵ the Hassé variational method[14] may be tried. We calculate

$$(H-E_0)\psi_0=-10\cos(132)\psi'(r_{13})\psi'(r_{23}) \quad (7)$$

and choose α in

$$\psi_1=\psi_0+\alpha(H-E_0)\psi_0 \quad (8)$$

in such a way that $(\psi_1, H\psi_1)$ assumes its minimal value

$$E_1=\tfrac{1}{2}E_0+V'/2V_2-[\tfrac{1}{4}(V'/V_2-E_0)^2+V_2]^{1/2} \quad (9)$$

where $E_0=(\psi_0, H\psi_0)=-2\epsilon$, $V_2=(\psi_0, (H-E_0)^2\psi_0)$ and $V'=(\psi_0, (H-E_0)^2H\psi_0)$. In the present case we have $V_2=(1/3)K^2$ where K is the mean kinetic energy in H^2. This is very large and shows that ψ_0 is certainly rather far from the correct wave function. As to E_1, however, as V' is even larger than $(V_2)^{3/2}$ it turns out that it is not far from the value $E_0=-2\epsilon$. It might be therefore that the second neutron is only somewhat (perhaps twice) as strongly bound as the first. The relative occurrence of H^3 would be therefore much rarer even than that of H^2, as usually an isotope with a mass number one larger than the other is very rare if the mass defect is so small. The magnitude of the mass defect and even the existence of the H^3 becomes uncertain of course, if we assume repulsive forces between the neutrons.

[13] This is, of course, not true for the third neutron as a wave function like (6) is not allowable for more than two neutrons in consequence of Pauli's principle. Actually if ρ is not too large, the third neutron has no positive binding energy.

[14] H. R. Hassé, Proc. Camb. Phil. Soc. **26**, 542 (1930).

IV.

We now come to the calculation of the binding energy of the He nucleus, 1 and 2 are neutrons, 3 and 4 protons. We may try as the first approximation to ψ the following expression

$$\psi_1=\frac{f(r_{13})f(r_{23})f(r_{14})f(r_{24})}{[\int f(r_{13})^2 f(r_{23})^2 d3]^{1/2}} \tag{10}$$

where $\int \cdots d3$ indicates integration over all coordinates of the particle 3 and f is an as yet unknown function which will later be taken as the solution of an equation similar to (2) but with a different V. The meaning of (10) is, that the probability $\int \psi_1^2 d3$ of a certain position of 4 for a given position of 1 and 2 is $f(r_{14})^2 f(r_{24})^2$, in analogy to (6). Really, ψ will be symmetric with respect to the interchange of the pair 1, 2 with the pair, 3, 4.

Upon calculating the expectation value of the potential energy for ψ_1, given by (10), one obtains $4\int f(r_{12})^2 V(r_{12}) d1d2 = 4P_f$, four times the mean potential energy of a nucleus H^2 in the state $\psi=f$. For the kinetic energy, however, one gets

$$4K_f - 10\int[\int \cos(314) f'(r_{14}) f(r_{14}) f'(r_{13}) f(r_{13}) f(r_{23})^2 f(r_{24})^2 d3d4 / \int f(r_{13})^2 f(r_{23})^2 d3]d1d2 \tag{11}$$

where

$$K_f = 10\int f'(r_{13})^2 d1d3 \tag{12}$$

is the mean kinetic energy of the proton and neutron in H^2 in the state $\psi=f$. The kinetic energy for (10) is, in consequence of (11), smaller than $4K_f$ as the integral in (11) is positive. One sees this by writing

$$\cos(314) = \cos(312)\cos(214) + \sin(312)\sin(314)\cos\alpha \tag{13}$$

where α is the angle between the planes through 1, 3, 2 and through 1, 3, 4. After inserting (13) into (11) one sees that the integral arising from the second part of (13) will vanish upon integration over α and the total integral in (11) becomes

$$\int \frac{(\int \cos(312) f'(r_{13}) f(r_{13}) f(r_{23})^2 d3)^2}{\int f(r_{13})^2 f(r_{23})^2 d3} d1d2 \tag{14}$$

which is clearly positive. This integral was estimated in the following way. The function $f(r)$ was approximated by $\alpha e^{-\beta r^2}$ with undetermined α and β. Then (14) was calculated and compared with the integral occurring in the expression (12) of the kinetic energy. It was found—as might be expected—that the ratio of both is independent from α and β and is equal to 0.5. For $f=\alpha e^{-\beta r}$ the ratio is even 0.64, but 0.5 was adopted in the subsequent calculation in order to stay on the safer side. The total energy therefore is for ψ_1

$$(\psi_1, H\psi_1) = 4P_f + 3.5K_f = 3.5(K_f + 1.14P_f). \tag{15}$$

Now we can choose f so as to minimize (15), which is readily obtained, by assuming that f is the solution of a differential equation like (2), only with the potential multiplied by 1.14. The total energy (15) is then 3.5 times the binding energy of such an imaginary nucleus, with 1.14 times the real attraction.

As was pointed out before, the characteristic value of (2) is under these conditions very sensitive to a small increase of the potential. For $\rho=0.22$, $v_0=140$ we obtain in this way a mass defect for the He, which is 7.85 times larger than that of the H^2.

One more improvement was made in this calculation: instead of ψ_1 the symmetrized function

$$\psi = \psi_1 + \psi_2 \tag{16}$$

with

$$\psi_2=\frac{f(r_{13})f(r_{23})f(r_{14})f(r_{24})}{[\int f(r_{13})^2 f(r_{14})^2 d1]^{1/2}} \tag{10a}$$

was taken as wave function. Then the expectation value for the energy becomes

$$\frac{(\psi_1, H\psi_1)+(\psi_1, H\psi_2)}{1+(\psi_1,\psi_2)} = \frac{A+B}{1+S}. \tag{17}$$

A is, according to (15), $4P_f+3.5K_f$. In order to calculate S and B, the function $f(r)$ was again approximated by $\alpha e^{-\beta r^2}$, which gave $S=0.84$ and $B=3.82P_f+2.80K_f$ so that in the whole we have

$$E = 3.45(K_f + 1.24P_f). \tag{18}$$

Minimizing (18) in the same way we get 12 for the ratio of the mass defect of He and H^2 in contrast with the observed value of about 17. This again corresponds to $\rho=0.22$ or a half-width of about $0.38e^2/mc^2$ for the potential hole. For larger ρ the ratio becomes smaller, for

smaller ρ larger. Another possibility is to take $\psi=(\psi_1\psi_2)^{1/2}$. This gives on a similar calculation $E=3.2(K_f+1.25P_f)$ for $\rho=0.22$ or a ratio of $11\frac{1}{2}$. Now one could take a linear combination of this ψ with that of (16), which would give a still somewhat lower value—not very much, however, because the two wave functions forming the linear combination do not differ very much from each other.[15]

There is, however, an other possibility to improve the wave function, namely to take advantage of the mixed differential coefficient terms in (5) as we did it for H^3 with the Hassé method. This would for the ρ under consideration, probably increase the ratio even somewhat over the experimental value.

It seems therefore that if the potential hole is thin, the attractive forces between the neutron and proton give even a too large mass defect for the He, so that a repulsion between the different neutrons and between the different protons may be assumed.

In conclusion one can state that if the basis of the present calculation should prove to be correct, the difference of the mass defects of He and H^2 can be attributed to the great sensitivity of the total energy to a virtual increase of the potential—as is brought about by the fact that every particle in the He is under the influence of two attracting particles, instead of one as in the case of H^2. The reason for this sensitivity lies in the functional dependence of the lowest energy value on a multiplicative factor v of the potential, which is as follows. For very small values of v there is no negative energy value at all (provided that the potential goes more strongly to zero than $1/r^2$). If v attains a critical value ($5/\rho^2$ for the potential (1)), there arises one discrete energy value at zero, which becomes more negative on a further increase of v. In the neighborhood of the critical value, however, a very large relative change corresponds to a comparatively small relative change of v. A characteristic property in the neighborhood of the critical value of v is that the mean kinetic energy is almost oppositely equal to the mean potential energy, i.e., the total negative energy is much smaller than the kinetic. That this is actually the case can be simply shown by an application of Heisenberg's indetermination principle.[16]

No similar sensibility exists, of course, in one dimension as the critical value of v is 0 in this case.[17]

[15] The best wave function I could find was $\alpha e^{-\frac{1}{2}\beta(r_{13}^2+r_{23}^2+r_{14}^2+r_{24}^2+\frac{1}{2}r_{12}^2+\frac{1}{2}r_{34}^2)}$, it gave a ratio of about 14.

[16] W. Heisenberg, reference 3, calculated in this way the kinetic energy of the electron in the neutron and inferred from the number obtained that it cannot obey the laws of quantum mechanics since the mean kinetic energy is much larger than the mass defect. This consideration, of course, cannot be applied for the free electrons in the higher nuclei (cf. reference 6) as the mass defects are much larger than that used by Heisenberg for the neutron, and the same holds also for the nuclear diameters.

[17] R. Peierls, Zeits. f. Physik **58**, 59 (1929).

Theory of the Dispersion and Absorption of Helium

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I. Herzfeld and Wolf were able to conclude from the behavior of the refractive index of helium in the visible spectrum that the continuous absorption of the gas below the 507A series limit plays an essential part in producing the observed refractivity. II. The present investigation involves a quantum mechanical calculation of the actual strength of this continuum, and also of the resonance line at 584A. As a by-product, the atomic absorption coefficient for x-rays is computed. III. The accuracy of the calculations is discussed. The 30 percent deviation from the present value of Vinti's value for the strength of the resonance line is accounted for. IV. The f sum rule is verified to 2 percent and the experimental refractive index is checked within 3 percent. V. It is discussed why the continuous spectrum is relatively so much stronger in helium than in hydrogen and the alkali metals.

I. INTRODUCTION

THE object of the present paper is to account for the refractive index of helium, as observed by C. and M. Cuthbertson,[1] by calculating the strengths f_i of the absorption frequencies ν_i appearing in the ordinary dispersion formula

$$n-1=(Ne^2/2\pi m)\Sigma_i f_i/(\nu_i^2-\nu^2). \qquad (1)$$

Here N is the number of atoms per cc, e and m are the electronic charge and mass, ν is the frequency of the incident light, and the ν_i are the absorption frequencies due to transitions from the ground state of the atom to higher energy levels. Even before any theory existed for the calculation of the f_i, Herzfeld and Wolf[2] were able to obtain some information as to their sizes and the position of the ν_i by considering only one or two terms of the infinite series (1), and adjusting the four disposable constants f_1, f_2, ν_1, ν_2, so as best to fit the experimental data. The absorption of helium is due to a line spectrum starting at 584A and running to a limit at 505A, and a continuous spectrum which starts at the series limit and extends to shorter wave-lengths. Their conclusion was that the contribution of the f's of the line spectrum is considerably outweighed by the effect of the f distributed over the continuous spectrum.

With quantum mechanics at his disposal, Vinti[3] has been able to compute approximate values for the f_i of the line spectrum of helium. The total effect of all the lines involving single electron jumps, he found, is at most 0.54; of all lines involving double jumps, at most 0.04. The f sum rule of Reiche, Kuhn, Thomas (see reference 11) says that the total electron number of helium is 2; thus Vinti could conclude that the integrated f of the continuous spectrum is at least 1.42. The accuracy of Vinti's work is discussed later (Section III). His most important contribution as far as the present work is concerned is the determination of an upper bound for the strength of double jumps.

In the following work double jumps are neglected, not only because they are weak, but also because their frequencies are so high that they contribute very little to the right side of Eq. (1). The error in the visible refractive index made by neglecting them is of the order of one percent or less. The number of excited states which need be considered is further reduced by the selection rules. Since the ground state of helium, $(1s)^2\ {}^1S$, is even singlet with orbital quantum number $L=0$ and magnetic quantum number $m=0$, it can make dipole transitions only to odd singlet states for which $L=1$: ${}^1P^0$. Further, according as the light is right or left handed circularly polarized or polarized parallel to the Z axis, the

[1] C. and M. Cuthbertson, Proc. Roy. Soc. **A135**, 40 (1932).

[2] K. F. Herzfeld and K. L. Wolf, Ann. d. Physik **76**, 71, 567 (1925).

[3] J. P. Vinti, Phys. Rev. **42**, 632 (1932). This paper appeared when the present work was being prepared for publication.

magnetic quantum number m of the excited state must be ± 1 or 0. The only such states which can be reached by jumps of a single electron are of the type $(1s, np)\ ^1P^0$. Below, the f value of the resonance line transition to $(1s, 2p)\ ^1P^0$ is calculated, as well as the f values for the continuous spectrum of $^1P^0$ levels beyond the series limit.

II. Calculation of Electron Numbers

The electron number or strength, f, of the transition from the S state with wave function φ to the triply degenerate P state with wave functions $\psi_m (m=-1, 0, 1)$ can be determined from the equation[3a]

$$f=(8\pi^2 m\nu/3h)\Sigma_m\{|X_m|^2+|Y_m|^2+|Z_m|^2\}.$$

Here m is the electronic mass, $h\nu$ the energy E_1-E_0 gained in the transition, and

$$Z_m=\int \varphi(z_1+z_2)\psi_m dV \qquad (2)$$

is the matrix element of the z component of the total electronic displacement. In what follows, the unit of energy is Rh (Rydberg's constant: $R=3.29\times10^{15}$/sec.), and the unit of distance is $h^2/16\pi^2 me^2$; that is, $a/4$, where $a=0.528\times10^{-8}$ cm is the Bohr radius for hydrogen. As a consequence of spherical symmetry and the choice of units,

$$f=Z_0^2(E_1-E_0)/16. \qquad (3)$$

As wave function for the ground state, the eigenfunction of Hylleraas[4] is used, the most accurate known for any atom except hydrogen:

$$\varphi=(8\pi^2)^{-\frac{1}{2}}F=(8\pi^2)^{-\frac{1}{2}}\exp(-kr_1-kr_2)\times(A+Br_1+Br_2+Cr_1^2+Dr_1r_2+Cr_2^2+Er_1r_2\cos\theta+Fr_{12}). \qquad (4)$$

Here r_1, r_2, and r_{12} are the distances of the two electrons from the nucleus and from each other, θ the angle between r_1 and r_2; $A=0.1922$, $B=-0.00485$, $C=0.00156$, $D=-0.00229$, $E=0.00076$, $F=0.0170$, $k=0.455$; the corresponding value of the energy E is -1.8065, as against the experimental value -1.8070. φ is a pure radial function; that is, it depends upon the size and shape of the triangle r_1, r_2, r_{12}, but not upon the orientation of this triangle in space.

The wave functions ψ_m for a $^1P^0$ state depend also upon the orientation in space of the triangle of charges; but, as Breit[5] has shown, in analogy to the case of hydrogen this angular part of the helium wave function may be split off to give a wave equation involving the radial part G:

$$\frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial G}{\partial r_1}\right)+\frac{1}{r_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial G}{\partial r_2}\right)+\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial G}{\partial\theta}\right)+\frac{2}{r_1^2}\left(\cot\theta\frac{\partial G}{\partial\theta}-G\right)-\frac{2}{r_2^2\sin\theta}\frac{\partial PG}{\partial\theta}+\left(\frac{1}{r_1}+\frac{1}{r_2}-\frac{1}{2r_{12}}+\frac{E-4}{16}\right)G=0. \qquad (5)$$

The permutation operator P above is defined by $PG(r_1, r_2, \theta)=G(r_2, r_1, \theta)$. G is to be normalized so that

$$\tfrac{2}{3}\int G(G+PG\cos\theta)r_1^2r_2^2\sin\theta dr_1dr_2d\theta=1. \qquad (6)$$

The complete wave function ψ_0 is connected with G by the relation

$$\psi_0=(8\pi^2)^{-\frac{1}{2}}[G\cos b+PG(\cos\theta\cos b-\sin\theta\sin b\cos c)]. \qquad (7)$$

The angles a, b, and c are the Euler angles used to describe the orientation of the triangle in space: a describes rotation about the Z axis, b is the angle between the Z axis and the radius vector to the first electron, and c indicates rotation about this radius. Eq. (5) is exact for both the resonance and the continuous levels.

The wave function for the resonance level $(1s, 2p)\ ^1P^0$ may be determined by the simple variational method used by Breit[6] in another

[3a] See, for example, Born and Jordan, *Elementare Quantenmechanik*, 1st edition, p. 247.

[4] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929). Hylleraas' function, given in elliptical coordinates, is re-expressed above in terms of r_1, r_2, and θ, and has been normalized by use of his normalization integral.

[5] G. Breit, Phys. Rev. **35**, 569 (1930).

[6] G. Breit, Phys. Rev. **36**, 383 (1930).

connection. If the term $1/r_{12}$ were absent in Eq. (5), the radial function G would be $r_1 \exp(-r_1/4-r_2/2)$. For the perturbed function a similar form is chosen, involving three adjustable constants, g, c, and a:

$$G(r_1, r_2, \theta) = h(gr_1 - c) \exp(-gar_1/2 - gr_2/2). \quad (8)$$

These constants are varied to make the value of the energy averaged over the state a minimum. The result is: $g=1.00$, $c=0.238$, $a=0.25$; the normalization factor $h=0.00397$; and the average value of the energy is -0.2447, as compared with the experimental value -0.2476 (measured in units Rh above ionization).

The wave functions for the continuum of energy levels beyond the series limit also satisfy Eq. (5), which is exact. An approximation for an excited function is secured by taking one electron (2) as bound in a $1s$ state acted upon only by the charge $2e$ of the nucleus, and the other electron (1) free (i.e., in a p hyperbolic orbit) and acted upon by a centralized charge of $2e-e=e$. The effect of this approximation is to replace the term $(1/r_1 - 1/2r_{12})$ in Eq. (5) by the term $1/2r_1$, the difference between the two falling off for large r_1 as r_2/r_1^2. The solution of the altered wave equation is the product of functions of r_1 and r_2 alone:

$$G(r_1, r_2, \theta) = N(E) \exp(-r_2/2) \oint \exp(ir_1 z/4)(z+E^{\frac{1}{2}})^{1+iE^{-\frac{1}{2}}}(z-E^{\frac{1}{2}})^{1-iE^{-\frac{1}{2}}} dz. \quad (9)$$

E is the energy above ionization. The representation of the function of r_1 through a complex integral, as well as the determination of the normalization factor

$$N(E) = 3^{\frac{1}{2}}(512\pi)^{-1}(1+E)^{-\frac{1}{2}}(1-e^{-2\pi E^{-\frac{1}{2}}})^{-\frac{1}{2}} \quad (10)$$

are carried out by the methods of Schrödinger[7] and Fues.[8] The function of r_1 must be defined by a complex integral or an infinite series because it cannot be expressed in finite terms through known (i.e., tabulated) functions. In the integration, z runs around a circle surrounding the two branch points $-E^{\frac{1}{2}}$ and $E^{\frac{1}{2}}$. It should be stated at this point that it is impossible in the continuous spectrum to normalize G so that $\int \psi_0^2(E) \times dV = 1$, because the probability of the free electron being at infinity is not zero. Instead, $N(E)$ is chosen (following Fues) so that

$$\int \psi_0(E) \int_{E-\Delta E}^{E+\Delta E} \psi_0(E')dE'dV = 1,$$

where ΔE is arbitrarily small. It is a consequence of this changed normalization that Eq. (3) gives for the continuous spectrum, not f, but df/dE.

Since the main part of the electron number of helium lies in the continuum, it is important to know how good is the approximate function given by Eq. (9). That function represents the outer electron moving in the field created by a charge of e at the nucleus; but is clear that when r_1 is small compared with the radius of the $1s$ orbit, the effective charge acting on the free electron will have increased to nearly $2e$. If it is assumed that the free electron does not influence the charge distribution of the $1s$ electron, the potential field $V(r_1)$ in which the free electron moves may be calculated:

$$r_1 V(r_1) = -\tfrac{1}{2} - \tfrac{1}{2}(1 + r_1 + \tfrac{1}{2}r_1^2) \exp(-r_1).$$

The effective charge $Z_{eff.} = -2r_1 V(r_1)$ is plotted in Fig. 1. The wave function for the free electron in this field of force may be found by numerical integration of the corresponding one-electron Schrödinger equation. The solution for $E=0.01$, multiplied by the radial density factor r_1, is shown by the curve He* in Fig. 1; and the corresponding solution for the original potential field $r_1 V(r_1) = -\frac{1}{2}$ is shown by the curve marked H*, which is the exact wave function for hydrogen for $E=0.01$. The normalization of the two curves is the same. For large values of r_1, the excited functions behave nearly as $\sin(E^{\frac{1}{2}}r + p)$. It is seen that the main effect of the change in field is to pull the waves in towards the nucleus. Curve He in Fig. 1 represents a sort of effective wave function for the ground state of helium, such that the matrix element Z_0 of the electron displacement is given by $\int \mathrm{He}\, r_1\, \mathrm{He}^* dr_1$, the integration over r_2 and θ having been performed. For the given value 0.01 of E, the electric moment calculated on the basis of the modified field

[7] E. Schrödinger, Ann. d. Physik 80, 437 (1926).
[8] E. Fues, Ann. d. Physik 81, 281 (1926).

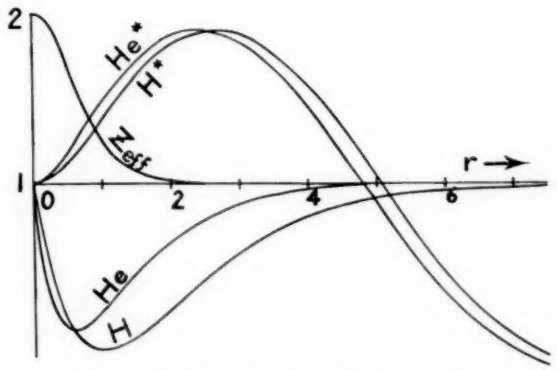

FIG. 1. $Z_{\text{eff.}}$, effective charge acting on excited electron of helium. H* and He*, excited wave functions of hydrogen and helium for $E=0.01$. H, ground function of hydrogen; He, "effective" ground function of helium (cf. Section II). r is in units of the Bohr radius. Functions are not normalized.

is about 5 percent greater than that calculated from the original field. Consideration of the free-electron wave equation shows that for large values of E the effect of the field change on the excited wave function will grow progressively less. Of course, the above discussion considers only the effect of the inner electron on the motion of the outer; but because this effect is so small, it may be considered that the converse effect will also be small. Accordingly, hydrogenic wave functions are used in the following calculations for the continuous spectrum.

The necessary eigenfunctions being known, the matrix element Z_0 may be calculated. As in the case of hydrogen, the whole integration reduces to a radial integral:

$$Z_0=\tfrac{2}{3}\int\int\int\int F(r_1, r_2, \theta)(r_1+r_2\cos\theta) \times G(r_1, r_2, \theta)r_1^2r_2^2\sin\theta dr_1dr_2d\theta. \quad (11)$$

For the resonance line, Z_0 is found to be 1.65; since $E_1-E_0=-0.247+1.807=1.56$, Eq. (3) gives 0.266 for the f value of the resonance line.

For the continuous spectrum, $E_1-E_0=1.807+E$. $Z_0(E)$ is found by integrating (11) first over θ, r_2, and r_1; then the integration with respect to the complex quantity z involved in G (Eq. (9)) may be carried out by the method of residues. The result is:

$$df/dE=Z_0^2(E)(1.807+E)/16=(1.807+E)(1+E)^{-1}(1-e^{-2\pi E^{-\frac{1}{2}}})^{-1}[(E+3.31)^{-5}(0.227E^5 +3.76E^4+66.3E^3+389E^2+1250E+943)\exp(-2E^{-\frac{1}{2}}\arctan(E^{\frac{1}{2}}/1.82))-(E+31.8)^{-3} \times(0.227E^3+19.9E^2+535E+3280)\exp(-2E^{-\frac{1}{2}}\arctan(E^{\frac{1}{2}}/5.64))]^2. \quad (12)$$

Values of df/dE calculated from this formula for several values of E are given in Table I. The variation of the electron number with the energy E of the excited level may be seen from Fig. 3, where there is plotted against the wave-length λ in A ($\lambda=911(1.807+E)^{-1}$) the closely related quantity α, the coefficient of linear absorption appearing in the ordinary intensity formula

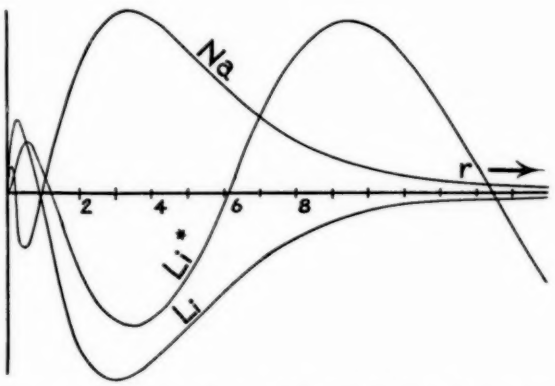

FIG. 2. Wave functions for the alkali metals, not normalized. Li and Na are ground functions; Li* is excited function for $E=0$. r in Bohr units. (Curves taken from B. Trumpy.)*

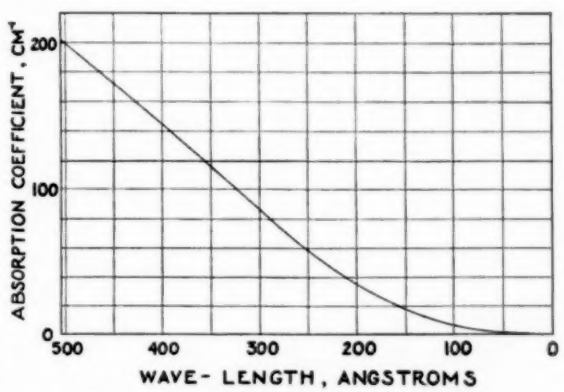

FIG. 3. Theoretical curve for the absorption coefficient of helium. (Cf. Section II.)

* B. Trumpy, Zeits. f. Physik **71**, 728 (1931), and **61**, 54 (1930).

TABLE I. *Electron number of helium.*
E is in units *Rh*.

E	*df/dE*	*E*	*df/dE*
0.0	0.93	3.0	0.146
0.2	0.81	3.5	0.116
0.4	0.70	4.0	0.093
0.6	0.62	5.0	0.065
0.8	0.53	6.0	0.046
1.0	0.47	7.0	0.033
1.3	0.38	8.0	0.026
1.6	0.31	9.0	0.020
2.0	0.25	10.0	0.015
2.5	0.19	16.0	0.0056

Total *f*. continuum: 1.58. *f* value, resonance line: 0.266.

$I = I_0 \exp(-\alpha x)$. In terms of f, at standard pressure and temperature,

$$\alpha = \pi Ne^2/(mc)df/d\nu = \pi Ne^2/(mcR)df/dE = 207(df/dE)\ (\mathrm{cm}^{-1}).$$

The only experiments made so far upon the strength of the continuous absorption of helium are not quantitative enough to compare with Fig. 3.[9]

The behavior of the electron number for large values of E may be found by expanding the exponentials in Eq. (12). For very short wave-lengths, $df/dE \sim 2.8\times10^{-8}\lambda^{3.5}$; consequently the "true" absorption coefficient τ_a for x-rays, per atom, is $2\times10^{-25}\lambda^{3.5}$. This formula cannot be expected to hold for wave-lengths less than, say, 5A, because above no account is taken of the difference in the phase of the incident radiation over the atom.

III. Accuracy of Calculations

The accuracy of the continuous wave functions has been discussed above. For $E=0.01$ the inaccuracy in the calculated value of the electron number is of the order of 10 percent, and decreases for increasing values of E.

The inaccuracies in the ground and excited function show up doubled in the electron number. Eckart[10] has shown that the error in a wave function obtained by variational means is of the order of $(\Delta E/(E_1-E_0))^{\frac{1}{2}}$. ΔE is the difference between the computed and correct energy values, and E_1-E_0 is the distance to the next higher energy level of the same spectral type. For the ground function (Eq. (4)), E_1-E_0 is 1.52 and ΔE is 0.00052, giving a percentage error of the order of two. For the resonance level wave function (Eq. (8)), E_1-E_0 is 0.137 and ΔE is 0.003, implying a percent inaccuracy of the order of 15. Thus the maximum error in the computed electron number $f=0.266$ of the resonance line is of the order of 30 percent. However, Vinti[3] obtains an f value of 0.349, 31 percent higher. It is probable that the difference between the two values arises mainly from the ground function which he uses; it gives an energy error ΔE of 0.052, implying a percent error of possibly 18 in the ground function, and a possible error of 60 percent in the electron number, since his resonance wave function has practically the same accuracy as the one used above.

IV. The *f*-Sum Rule and Refractive Index

The sum rule of Reiche, Kuhn and Thomas[11] demands that the total electron number of helium be 2. From formula (12) the contribution of the continuum to f was found to be 1.58. For the resonance level $f=0.266$. The strength of the other lines in the same spectral series $(1s, np)\ ^1P^0$ may be estimated from the formula valid asymptotically for large n : $f_n \alpha 1/n^3$.[12] This gives as the contribution of the rest of the series $0.266 \times 2^3 \times \sum_{n=3}^{\infty} 1/n^3 = 0.159$. Summing up, the total f is $1.58+0.266+0.159=2.00$. This is slightly too large, for Vinti estimates that double jumps contribute of the order of 0.04 to f.

The electron number being known, the refractive index can be calculated from Eq. (1), and compared with experiment. Frequencies lying in the visible spectrum are so small compared with the absorption frequencies that the structure of the latter does not show up; this is why Cuthbertson can represent his measurements by means of a one term formula:

$$n-1 = 1.32614\times10^{27}/(3.83137\times10^{31}-\nu^2). \quad (13)$$

The mean or effective absorption frequency in

[9] See, for example, C. Cuthbertson, Proc. Roy. Soc. **A114**, 650 (1927).

[10] C. Eckart, Phys. Rev. **36**, 878 (1930).

[11] W. Kuhn, Zeits. f. Physik **33**, 408 (1925).

[12] Hartree, Proc. Camb. Phil. Soc. **25**, 75 (1929).

this formula lies at 485A. To simplify comparison of theory with experiment, choose the constants A and F in the equation

$$n-1=(Ne^2/2\pi m)A/(R^2F^2-\nu^2)$$

so that at some convenient frequency Re, lying in the midst of Cuthbertson's observations, this one term approximate formula has the same ordinate and slope as the right-hand side of Eq. (1). Take $e=0.25$, corresponding to 3644A. F and A are given by $F^2-e^2=I/J$; $A=I^2/J$; here

$$I=\int\frac{df(E)}{(E-E_0)^2-e^2};\quad J=\int\frac{df(E)}{((E-E_0)^2-e^2)^2}.$$

(This Stieltjes integral cares for both line and continuous spectrum). The f values calculated above for the continuum and the resonance line, together with the values derived for the series $(1s, np)^1P^0$ by means of the $1/n^3$ law give for A, the effective electron number, 1.27; and for F, the effective frequency, 1.89, corresponding to 482A. The corresponding one term formula is

$$n-1=1.38\times10^{27}/(3.865\times10^{31}-\epsilon^2). \quad (14)$$

There is 3 percent difference between this formula and Cuthbertson's (Eq. (13)).

V. Discussion

There are two independent checks on any calculation of f values: the f sum rule and the experimental refractive index. The fact that one criterion is fulfilled to 2 percent and the other to 3 percent makes it possible to conclude that the actual error in the electron number calculations is much less than the possible error indicated in Section III, and that the refractive index of helium is satisfactorily accounted for by theory.

The question arises as to why the continuous spectrum of helium is so much stronger than that of the hydrogen-like elements (cf. Table II). The strength of the absorption varies as the square of the matrix element of the electric moment. To give an indication why this matrix element is larger for helium than for other atoms, the ground and excited wave functions of several atoms are shown (unnormalized) in Figs. 1 and 2, each multiplied by the density factor r. To obtain the matrix element, the factor r must be used again: $Z=\int ArA^*dV$, for an atom A. The immediate neighborhood of the nucleus contributes very little to this integral; and the essential part of the excited function varies only slightly from atom to atom. The important variation occurs in the ground function. The maxima of all the curves occur at larger values of r than the maximum of the helium ground function; and this shift to larger values of r is such that an important interference effect takes place in the formation of the matrix element integral except in the case of helium. That is to say, the integrand oscillates above and below zero with increasing r because of the excited function; this oscillation has died out with helium at the first half wave; but with hydrogen, and more especially with sodium and lithium, the oscillation falls off more slowly, and the positive and negative parts of the integrand to a considerable extent annul one another. Thus the essential factor is the relation between the wave-length of the free electron and the radius of the atom.

Table II. *Strength of ultraviolet absorption.*

Atom	Total f of continuum	df/dE, series limit	Reference
H	0.437	0.78	Suguira[13]
He	1.58	0.93	Present paper
Li	0.24	0.46	Trumpy[14]
Na	0.0021	0.038	Trumpy[15]
K		0.0024	Phillips[16]

The author is indebted to Professor Herzfeld for suggesting the foregoing problem, and is very grateful to him for the advice received in working it out.

[13] Sugiura, J. de Physique **8**, 113 (1927).
[14] B. Trumpy. Zeits. f. Physik **54**, 373 (1929).
[15] B. Trumpy, Zeits. f. Physik **71**, 720 (1931).
[16] M. Phillips, Phys. Rev. **39**, 905 (1932).

The Interaction of Configurations: $sd - p^2$

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It does not seem possible to account for the presence of singlets below their triplets in two electron spectra simply from the ordinary exchange integrals. The exchange integrals seem to be essentially positive. It is shown that the matrix component of electrostatic energy connecting the $3s\,3d\,{}^1D$ with $3p^2\,{}^1D$ in Mg I is sufficiently large to account for the occurrence of $3s\,3d\,{}^1D$ below $3s\,3d\,{}^3D$ as observed experimentally. Analytic radial wave functions of the type developed by Slater are used in the calculation of the nondiagonal elements.

THE spectra of elements and ions which contain two valence electrons outside closed p or d shells, are in general quite regular. That is, the energy states are for the most part those for which one electron remains in a low s-state and the other takes on higher values of n and l. The resultant states are singlet and triplet terms with the L determined from the second electron. For some of the heavier elements which follow the completion of a d-shell there are many other terms which arise when one of the d-electrons is excited from its closed shell. The presence of these states causes large perturbations in the singlets and triplets, disturbing both their multiplet separations and their series. These perturbations are for the greater part quite complicated. If one considers only those cases for which only the two electrons are excited, the theory of Houston[1] is expected to hold. Condon and Shortley[2] have gathered together many examples of two electron spectra to see how they fit Houston's theory. The radial integrals which are involved in the theory are not calculated but are carried through as parameters for which certain relations are expected to hold from the theory. The radial integral of type (1) which gives the singlet-triplet separation is considered to be either positive (triplet below singlet) or negative (triplet above singlet). Condon and Shortley's work shows that for the cases for which the singlet is below the triplet there is very poor agreement with the theory.

In studying these difficulties for the D terms of Mg I which is one of the simplest cases where the singlet lies below the triplet, it was found that with no reasonable radial functions for magnesium could the singlet ever be expected to come below the triplet. The singlet-triplet separation is given by the following expression:

$$\frac{1}{5}e^2\int_0^\infty dr_1 R(3s, r_1)R(3d, r_1)\int_0^\infty dr_2 \frac{r_a^2}{r_b^3}R(3s, r_2)R(3d, r_2), \quad (1)$$

where $R(3s)$ and $R(3d)$ are one electron wave functions multiplied by r, and r_a is the smaller of r_1 and r_2, and r_b the larger. Fig. 1 gives a plot of these two wave functions as determined by the method of Slater. The negative contribution to the first integral arises from the second maximum of the $3s$ which has the opposite sign from the $3d$ wave function. This part is quite small; in fact one may get a good first approximation to the

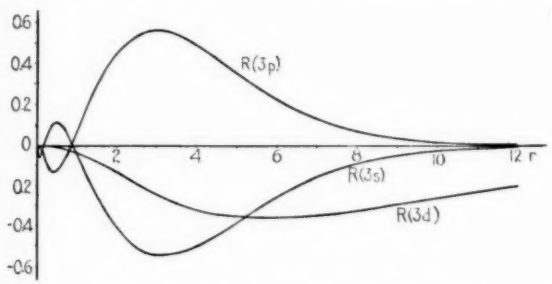

FIG. 1. $R(3p)$, $R(3s)$ and $R(3d)$ of Mg I as determined by the Slater method are plotted against r, where r is in units of the radius of the first Bohr orbit.

* Alfred Lloyd Fellow. The greater part of this work was carried out while the writer was National Research Fellow at the Massachusetts Institute of Technology.

[1] W. V. Houston, Phys. Rev. **33**, 297 (1929).

[2] E. U. Condon and G. H. Shortley, Phys. Rev. **35**, 1342 (1930).

integral by considering only the term in r^3 which gives the outer maximum of the $3s$ radial function. The same of course holds for the second integral. In other cases the first integral may be negative but then the second will be negative too and the product positive. This conclusion is a consequence of the position and relative magnitudes of the maxima of the radial wave functions and in general to get a negative integral would require very large and improbable distortions of the wave functions from hydrogen functions. It seems then that the examples of two-electron spectra for which the singlet lies below the triplet should not be expected to agree with the Houston theory and their explanation must lie elsewhere. It will be shown that perturbations by other configurations may be sufficiently large to account for them.

As pointed out by Condon,[3] the interaction between configurations often becomes so large that it is necessary to consider both configurations together as one in calculating the various matrix components. Condon pointed out that this happens when two configurations of the same parity overlap. This interaction may also be very large under favorable circumstances even in case the configurations are well separated.

The lowest of the configurations arising when both of the valence electrons of two electron spectra are excited is the p^2 configuration, but it seemed at first that it was quite unlikely that perturbations from this configuration could be causing the irregularity of the ordinary singlets and triplets, due to the fact that in some of the examples where the irregularity of the D terms is noted the p^2 levels are so much higher than this D level that they lie above the first ionization potential. Such an explanation seems to be the only one remaining, however, and this seems to be an indication that such interactions are very much larger in many cases than they have generally been supposed to be. The examples of the sd configuration which give the singlet below the triplet constitute the majority of such cases for two electron spectra, as would be expected if one considers that the even configuration p^2 lies very much lower than other configurations involving two excited electrons. This configuration does not perturb the sp and sf configurations because of the difference in parity and affects the ss configurations only in a lesser degree particularly in view of the larger "normal" triplet-singlet separation of the latter.

The Energy Matrices

If one includes both the electrostatic interaction and the spin-orbit interaction the Hamiltonian may be written as usual in the following form:

$$H=\sum_{\text{electrons}}\left[\frac{1}{2\mu}(p_x^2+p_y^2+p_z^2)-\frac{Ze^2}{r}+V(r)(l\cdot s)\right]+e^2\sum_{\text{pairs}}\frac{1}{r_{12}},$$

where the first sum is a sum of functions for each electron alone and the second for pairs of electrons. Since there are no components of H between states with different M_J it will be sufficient to consider only those of a single M_J value. In addition since, for Mg I and other simple cases the triplet is unaffected (the interval rule still holds), it will be sufficient to consider $M_J=2$, the largest value of M_J for which the singlet is represented and of course the simplest to treat. Furthermore after the transformation to $(L$–$S)$ wave functions the electrostatic energy in which we are particularly interested will have components only between states having the same L and S.

There are three states from the sd configuration and two from the p^2 included in the group $M_J=2$; ${}^3D_{3,2}$ ${}^1D_2$ and ${}^3P_2$ ${}^1D_2$, respectively. These five states have the m_s and m_l values for each electron and also resultant values for both electrons M_S and M_L as given in Table I. The diagonal and nondiagonal matrix compon-

Table I.

	s	d	M_S	M_L
1	$(\frac{1}{2}, 0)$	$(\frac{1}{2}, 1)$	1	1
2	$(-\frac{1}{2}, 0)$	$(\frac{1}{2}, 2)$	0	2
3	$(\frac{1}{2}, 0)$	$(-\frac{1}{2}, 2)$	0	2
4	$(\frac{1}{2}, 0)$	$(\frac{1}{2}, 1)$	1	1
5	$(-\frac{1}{2}, 1)$	$(\frac{1}{2}, 1)$	0	2
	p	p		

[3] E. U. Condon, Phys. Rev. **36**. 1121 (1930).

ents of H for these states are determined from expressions of the sort obtained by Condon[3] and by Slater, in terms of wave functions built up as Slater[4] did from one-electron wave functions. These will be referred to as the original wave functions. For convenience put $-Ze^2/r=H_1$; $V(r)(l\cdot s)=H_2$; and $e^2\ 1/r_{12}=H_3$. The matrix of H_3 has the following form in the original wave functions (see Table II) where the R's are various radial integrals.

TABLE II. *Matrix of H_3 in original wave functions.*

	1	2	3	4	5
1	$R_a-\frac{1}{5}R_b$	0	0	0	0
2	0	R_a	$-\frac{1}{5}R_b$	0	$(\frac{2}{175})^{\frac{1}{2}}R_c$
3	0	$-\frac{1}{5}R_b$	R_a	0	$(\frac{2}{175})^{\frac{1}{2}}R_c$
4	0	0	0	$R_d-\frac{1}{5}R_e$	0
5	0	$(\frac{2}{175})^{\frac{1}{2}}R_c$	$-(\frac{2}{175})^{\frac{1}{2}}R_c$	0	$R_d+\frac{1}{245}R_e$

$R_a=R^0(3s,\ 3s;\ 3d,\ 3d)$; $R_b=R^2(3s,\ 3d;\ 3d,\ 3s)$

$R_c=R^1(3s,\ 3p;\ 3d,\ 3p)$; $R_d=R^0(3p,\ 3p;\ 3p,\ 3p)$

$$R_e=R^2(3p,\ 3p;\ 3p,\ 3p),$$

where

$$R^k(\alpha,\beta;\gamma,\delta)=e^2\int_0^\infty dr_1\int_0^\infty dr_2 R_\alpha(r_1)R_\gamma(r_1)\frac{{r_a}^k}{{r_b}^{k+1}}R_\beta(r_2)R_\delta(r_2).$$

H_1 has only diagonal components which are the same for all *sd* states and again for all p^2 states. H_2, the magnetic interaction, has the form given in Table III. a and b are radial integrals depending on the form of $V(r)$. For the case of light elements both a and b are sufficiently small to be neglected in comparison to the much larger terms in H_1 and H_2.

TABLE III. *Matrix of H_2 in original wave functions.*

	1	2	3	4	5
1	$\frac{1}{2}b$	0	b	0	0
2	0	b	0	0	0
3	b	0	$-b$	0	0
4	0	0	0	$\frac{1}{2}a$	$\frac{1}{2}a$
5	0	0	0	$\frac{1}{2}a$	0

In order to be able to assign L and S values to the various states it is useful to have these energy matrices in terms of $(L-S)$ wave functions. To do this, matrices for L^2, S^2 and $L\cdot S$ are written down from the work of Johnson[5] and the transformation to make all three diagonal is found in the same manner as his. The transformation matrix is given in Table IV. After the transformation to $(L-S)$ wave functions H_3 and H_2 are given in Tables V and VI.

TABLE IV. *Transformation matrix.*

	1	2	3	4	5
1	$(\frac{2}{3})^{\frac{1}{2}}$	$(\frac{1}{6})^{\frac{1}{2}}$	$(\frac{1}{6})^{\frac{1}{2}}$	0	0
2	$-(\frac{1}{3})^{\frac{1}{2}}$	$(\frac{1}{3})^{\frac{1}{2}}$	$(\frac{1}{3})^{\frac{1}{2}}$	0	0
3	0	$(\frac{1}{2})^{\frac{1}{2}}$	$-(\frac{1}{2})^{\frac{1}{2}}$	0	0
4	0	0	0	1	0
5	0	0	0	0	1

TABLE V. *Matrix of H_3 in $(L-S)$ wave functions.*

	$^3D_3$	$^3D_2$	$^1D_2$	$^3P_2$	$^1D_2$
$^3D_3$	$R_a-\frac{1}{5}R_b$	0	0	0	0
$^3D_2$	0	$R_a-\frac{1}{5}R_b$	0	0	0
$^1D_2$	0	0	$R_a+\frac{1}{5}R_b$	0	$2(\frac{1}{175})^{\frac{1}{2}}R_c$
$^3P_2$	0	0	0	$R_d-\frac{1}{5}R_e$	0
$^1D_2$	0	0	$2(\frac{1}{175})^{\frac{1}{2}}R_c$	0	$R_d+(\frac{1}{245})R_e$

TABLE VI. *Matrix of H_2 in $(L-S)$ wave functions.*

	$^3D_3$	$^3D_2$	$^1D_2$	$^3P_2$	$^1D_2$
$^3D_3$	b	0	0	0	0
$^3D_2$	0	$-\frac{1}{2}b$	$(\frac{3}{2})^{\frac{1}{2}}b$	0	0
$^1D_2$	0	$(\frac{3}{2})^{\frac{1}{2}}b$	0	0	0
$^3P_2$	0	0	0	$\frac{1}{2}a$	$(\frac{1}{2})^{\frac{1}{2}}a$
$^1D_2$	0	0	0	$(\frac{1}{2})^{\frac{1}{2}}a$	0

H_1 is, of course, still diagonal. The only non-diagonal matrix component in H_3 which now ap-

[4] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[5] M. H. Johnson, Phys. Rev. **39**, 197 (1932).

pears is that between the two singlet D's. H_3, however, now contains several radial integrals which it is necessary to evaluate before going further. This may be simplified considerably in any particular case by calculating only those elements in which we are particularly interested and taking the rest from the experimental material. For example H_1 and the R_a and R_d terms of H_3 determine only the centers of gravity of the two electron configurations sd and p^2 and for the purpose of this work this may be taken from experimental material. There remain three radial integrals in H_3 and two in the magnetic interaction matrix. These last demand a knowledge of $V(r)$ for their evaluation and this function is known only very approximately. Fortunately for the cases of the lighter elements which compose many of the cases where the interaction between configurations may be simplified to the extent adopted here, the magnetic interactions are small compared to the electrostatic and may be neglected in first approximation.

The Radial Integrals

In order to determine the energy matrix H_3 it is necessary to evaluate the radial integrals and this involves knowledge of the radial wave functions for each particular atom considered. Slater[6] has recently given a method for obtaining analytic expressions to represent the Hartree wave functions, and this may be done with great accuracy. A method of interpolation provides wave functions for those atoms for which Hartree has not yet obtained functions. Unfortunately the Hartree functions have not been obtained for the optical electrons and to find wave functions for these electrons demands an extrapolation of Slater's curves which, while it does not give wave functions of as great accuracy as for the inner electrons, still gives greater accuracy than could previously be obtained. Mg I furnishes a good case for comparison with the experimental material. The radial functions given by the Slater method and normalized to unity are: (see Fig. 1)

$$R(3s) = (1/2.84)(-r^3e^{-0.95r} + 11.96r^2e^{-3.92r} - 6.86re^{-11.70r})$$

$$R(3d) = (10^{-3}/1.046)(-r^3e^{-0.70(r-5.71)} - r^3e^{-0.35(r-5.71)})$$

$$R(3p) = (1/2.37)(r^3e^{-1.00r} - 10.43r^2e^{-3.90r}).$$

For these radial integrals it is sufficient to consider only the terms in r^3, since the other terms have such high negative exponentials and thus contribute only for small r. Since r enters the integrals to a high power this makes the contribution from the terms with high exponentials small.

Experimentally the absolute energy states of Mg I for $3s\ 3d$ and $3p^2$ have been found to be $3s\ 3d\ {}^1D = 15{,}268.9\ {}^3D = 13{,}714.7$ (not separated) and $3p^2\ {}^3P_{0,1,2}$ to be 3860.4, 3839.6 and 3799.0 cm^{-1}, respectively. The ^1D from $3p^2$ has been reported by Sawyer[7] but this as pointed out by Paschen[8] is located too near the triplet. Furthermore, the regularity of the Rydberg denominators convinces one that it is a higher member of the $3s\ nd$ series. The failure of Paschen to find $3p^2\ {}^1D$ may well be due to its great displacement by the perturbation. Knowing the ^3D and ^3P however from experiment, it is sufficient, with the knowledge which can be obtained from the radial integral R_b and R_e to determine the parts of the electrostatic energy matrix which are the same for all terms from the same configuration (see Fig. 2a). Calculation of the radial integrals gives $R_b = 10{,}190\ cm^{-1}$, $R_c = 25{,}620\ cm^{-1}$; $R_e = 29{,}940\ cm^{-1}$, and the difference between the centers of the configurations determined as above is 13,845 cm^{-1}. The electrostatic energy matrix now becomes if we take sd as zero energy for convenience: (Table VII). This energy matrix leads to the following energy values: $^3D_{3,2}$ at $-2038\ cm^{-1}$, $^3P_2$ at $7857\ cm^{-1}$ and $^1D_2$ at $-6202\ cm^{-1}$ and $+23{,}282\ cm^{-1}$. This places one singlet D at $4000\ cm^{-1}$ below the triplet, a much larger displacement even than is found in experiment. Numerically this is not very good agreement but the difference may easily be due to the extrapolations made in determining the coefficients for the radial wave func-

[6] J. C. Slater, Phys. Rev. **42**, 33 (1932).

[7] R. A. Sawyer, J. Opt. Soc. Am. **13**, 431 (1926).

[8] F. Paschen, Sitz. Ber. Preuss. Akad. **32**, 709 (1931).

TABLE VII. *Matrix for H_3.*

	$^3D_3$	$^3D_2$	$^1D_2$	$^3P_2$	$^1D_2$
$^3D_3$	−2038	0	0	0	0
$^3D_2$	0	−2038	0	0	0
$^1D_2$	0	0	2038	0	13230
$^3P_2$	0	0	0	7857	0
$^1D_2$	0	0	13230	0	15043

tions. It is indicated, however, that even for such a case as magnesium for which the p^2 configuration occurs at the ionization potential, the perturbing effect on the *sd* configuration may be large enough to displace the ^1D to a position below ^3D.

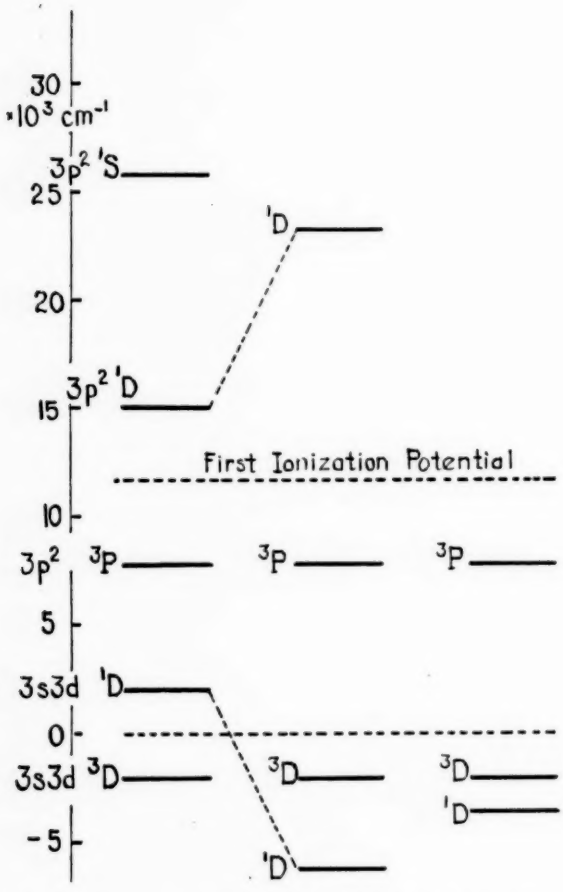

FIG. 2. Energy levels of $3p^2$ and $3s\ 3d$ of Mg I (a) without considering interaction of configurations, (b) with interaction of $3s\ 3d$ and $3p^2$ considered, (c) from experimental material. $^3P-^3D$ is taken from experiment in *a* and *b*.

PERTURBATION OF THE SERIES *s nd*

In order to find how the higher series members are perturbed it is necessary to know the energy matrices of p^2 and *s nd* considered together and also a matrix giving all the *s nd* members to see if the various series members disturb each other. This becomes very complicated when all the series members are considered, and as an approximation only the first two series members will be considered. The matrix of H_3 of $s(n+1)d$ and p^2 is the same as that of *s nd* and p^2 in form and differs only in the fact that $R(n+1)d$ is used in place of $R(nd)$ in determining the various radial integrals. For *s nd* and $s(n+1)d$ considered together H_3 has the following form when transformed to $L-S$ wave functions (see Table VIII). There are components only between like terms in the two configurations. Whether the disturbing effect is much greater between the singlets than between the triplets depends on the size of R_B. A comparison between this matrix and that for $s(n+1)d$ and p^2 taken together would allow one to determine whether perturbation of a series takes place by the perturbing configuration disturbing each configuration of the series separately or only one member of the series is disturbed and this disturbs the others. Since R_B is expected to be positive, any contribution from it would tend to increase the normal singlet triplet separation of the higher series member. This indicates that the perturbation of a series of terms such as those discussed by Shenstone and Russell[9] is caused by the separate perturbation of the series members by the perturbing configuration. A calculation of these effects for Mg I indicated that $R(4d)$ was not known with sufficient accuracy to give much significance to the results.

CONCLUSION

It thus seems that it is possible to account for the presence of singlets below their triplets in the two electron spectrum of Mg I by considering the perturbing effect of the low $3p^2$ configuration. It is believed that other examples, Al II, Zn I, Ga II, In II, and others which are similar to Mg I can also be accounted for in this way if the radial

[9] A. G. Shenstone and H. N. Russell, Phys. Rev. **39**, 415 (1932).

TABLE VIII. *Matrix of H_3 for s nd and s (n+1)d.*

		$s\ nd$			$s(n+1)d$	
	$^3D_3$	$^3D_2$	$^1D_2$	$^3D_3$	$^3D_2$	$^1D_2$
$^3D_3$	$R_a-\frac{1}{5}R_b$	0	0	$R_A-\frac{1}{5}R_B$	0	0
$s\ nd\ ^3D_2$	0	$R_a-\frac{1}{5}R_b$	0	0	$R_A-\frac{1}{5}R_B$	0
$^1D_2$	0	0	$R_a+\frac{1}{5}R_b$	0	0	$R_A+\frac{1}{5}R_B$
$^3D_3$	$R_A-\frac{1}{5}R_B$	0	0	$R_a'-\frac{1}{5}R_b'$	0	0
$s\ (n+1)d\ ^3D_2$	0	$R_A-\frac{1}{5}R_B$	0	0	$R_a'-\frac{1}{5}R_b'$	0
$^1D_2$	0	0	$R_A+\frac{1}{5}R_B$	0	0	$R_a'+\frac{1}{5}R_b'$

functions are known. There are undoubtedly many other cases where these large interactions of configurations are important and indeed they may account for many of the deviations which have been found from the Slater theory. It seems possible that these interactions may even be large enough to account for the inversion of doublets in alkali spectra as suggested by White.[10]

It is a pleasure to the writer to thank Professor Slater for his interest and criticism as well as for furnishing the radial functions.

[10] H. E. White, Phys. Rev. 40, 316 (1932).

On Cooperative Phenomena

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The study is proposed of a group of phenomena so far not systematically treated. The term cooperative phenomena is adopted because of the fact that these phenomena are caused by interactions of a great number of elementary particles such as electrons, atoms, etc. These interactions extend over distances which are enormously greater than the usual action radii of the elementary particles. A brief survey of some possible cooperative phenomena in static and in stationary systems is given and their importance in physics, astrophysics, and biology is pointed out. Incidentally a *generalization* of *thermodynamics* from static systems to stationary systems is discussed. The view is advanced that the existence of crystals is due to certain cooperative phenomena which fact would in general necessitate the existence of a *secondary structure of crystals*. The various general contentions and conclusions of this paper are illustrated and applied in the case of *ferromagnetism*.

§1. Introduction

A CRUDE survey shows that some of the major problems of modern physics may be roughly classified into four groups. These are: (1) The problem of the nuclei of atoms and the existence of elementary particles such as the proton, the electron and the photon; (2) the problem of the interaction of the electromagnetic and the gravitational fields with matter and the problem of unifying the fields; (3) the problem of the universe as a whole; (4) the problem of *cooperative actions* of a great number of elementary particles, and, in particular, the *problem of the solid state.*

The first three problems will probably necessitate radical changes of our current notions about time, space, causality, fields, etc. The fourth problem is of an entirely different nature inasmuch as it seems that no fundamentally new laws must be invented for its solution. The difficulty rather lies in our present inability to visualize the simultaneous cooperation of a great number of particles and the lack of mathematical methods to obtain exact solutions for sufficiently general cases of interactions between many elementary particles.

§2. General Types of Cooperative Phenomena in Static Systems

I do not make any claim to give a complete list of all possible cooperative phenomena with the following enumeration. The purpose of this investigation rather is to point out a few characteristic examples and to indicate what rôle they actually play or eventually might play in our attempt to comprehend in a scientific way the phenomena around us.

A. Cooperative phenomena caused by the special laws of force which govern the interaction between elementary individual particles

The special group of phenomena which is discussed in this section is closely related to the problem of the existence of equations of state in the thermodynamic sense. It is indeed well known that not every homogeneous physical system which is in thermal equilibrium allows of an equation of state. For example, for a space charge of equally charged particles there exists no universal relation between the pressure, the density and the temperature at a given point.

In order to formulate the conditions which are necessary to insure the existence of an equation of state we first must define what an equation of state is. In thermodynamics we distinguish between *extensive* and *intensive* quantities. Intensive quantities may be obtained by measurements in the immediate neighborhood of the point for which they shall be determined. Density, pressure, temperature, etc., are intensive properties. The value of an extensive property, on the other hand, can be determined only by measurements on the whole system. *An equation of state is a relation between intensive properties exclusively.* No

such relation exists, rigorously speaking, for any real system. We must, however, consider the following approximation. If S is the surface of our system, V its total volume and d a length of the order of the size of a molecule we usually neglect terms of the order Sd/V compared with one. Within this approximation many equations of state exist.

Suppose now that the system which we consider is built up of particles whose mutual energy $\Phi(r, \psi, \vartheta)$ as a function of the mutual distance r and polar angles ψ and ϑ is given by

$$\Phi(r, \psi, \vartheta) = a_0(\psi, \vartheta)r^{-p} + a_1(\psi, \vartheta)r^{-(p+1)} + \cdots. \quad (1)$$

The total potential energy ϵ_P of a particle in our system will be

$$\epsilon_P = \int \Phi(r, \psi, \vartheta) r^2 \sin \vartheta d\psi d\vartheta dr. \quad (2)$$

The integration must be extended over the whole system Σ. Carrying out the integrals over ψ and ϑ we obtain

$$\epsilon_P = A_0 \int dr/r^{p-2} + A_1 \int dr/r^{p-1} + \cdots. \quad (3)$$

From this equation it is evident that $p=3$ represents a critical value inasmuch as the first *integral converges* for an infinitely expanded system only if

$$p > 3. \quad (4)$$

It may of course happen that A_0 or some of the other coefficients are zero, which case will be discussed later. For $p<3$ the contribution of all particles in a shell between r and $r+dr$ to ϵ_P increases with r. In this case the energy ϵ_P depends very much on the boundaries of our system and no equation of state can exist. For $p>3$ an equation of state as we have defined it exists.

From these considerations it follows that for $p>3$ the *individual actions* between neighboring particles play the most important rôle whereas for $p<3$ we may say that the *cooperative actions between all the particles* are essential for the final equilibrium of the system.

The special group of cooperative actions discussed here is related to the fact that there are important cases with potential energy functions (1) for which

$$p \leq 3. \quad (5)$$

As mentioned already, a system made up of charges e_i of one sign only, that is an electron cloud or an ion cloud, is a system belonging to this class. We have here

$$\Phi_{ik}(r) = e_i e_k / r_{ik} \quad \text{with} \quad p = 1. \quad (6)$$

It is well known that no equation of state exists in this case. The pressure in a given point depends not only on the density and the temperature at this point but is greatly influenced by the boundary conditions.

It is also known that for an assembly of electrons the quantum theory postulates an *exclusion principle*. No two electrons in the system may have identical sets of quantum numbers. This means in other words that every electron of the system "knows" what every other electron is doing. This is equivalent to some kind of cooperative action between all the electrons of the system. Whether and how this action is related to the one mentioned above, which is due to $p=1$ is as yet unknown. It is certain, however, that these two cooperative actions play a great rôle for our understanding of the structure of matter.

There is another very important case for which $p=1$. Indeed according to the theory of relativity the structure of the universe as a whole is essentially determined by the gravitational interaction of all the matter which it contains. Again no equation of state can exist, a fact which in many respects complicates the problem of the universe as a whole very much.

It is well known in astrophysics that if gravitation is involved the entropy of an adiabatically closed system does not necessarily increase but may decrease in course of time. Take for instance the case of two big spheres of a monoatomic gas (Emden spheres) which are initially at two different temperatures T_1 and T_2. The sphere S_1 at the higher temperature T_1 radiates energy to the sphere S_2 of the lower temperature T_2. S_2 expands and T_2 is lowered in spite of the absorption of energy. On the other hand, T_1 increases because of the resulting contraction of S_1. This illustrates that if cooperative phenomena are involved ordinary thermodynamics may not be applicable.

A system which is built up of neutral elementary particles usually possesses an equation of state if the gravitational interactions may be

neglected. Indeed the next possible term in the expansion (1) is characterized by $p=3$. This term corresponds to the interaction of two dipoles μ. If we consider the dependency on r alone it is

$$\Phi(r) \propto \mu^2/r^3. \tag{7}$$

At the absolute zero point of temperature this would produce, according to (2), a potential energy ϵ_P per dipole which is proportional to $\log D$, if D is of the order of the linear dimensions of our system. In general, however, the temperature agitation makes two sufficiently distant dipoles practically rotate at random with respect to each other which causes ϵ_P to decrease rapidly enough with the distance to guarantee the existence of an equation of state. This happens for instance in a so-called dipole gas which possesses an equation of state. It also may happen that a particular line-up of the dipoles in space is characterized by a coefficient A_0 equal to zero. In this case the *integral* (2) *is conditionally convergent* and an equation of state may exist because of certain particular circumstances which are related to the formation of a so-called secondary structure. This will be elaborated upon later.

B. Cooperative phenomena which are produced by self-perpetuating electric or magnetic fields

The type of phenomenon which belongs in this group is best illustrated by the following simple example. In a uniformly electrically polarized isotropic medium which has the shape of a long needle the polarization P sets up a so-called Lorentz field $L=4\pi P/3$. If the dielectric constant of the medium is great enough, L may cause the *electric moment* P to be *self-perpetuating*. This polarization causes either the atoms to be stripped of their electrons[1] or it may produce permanent electric moments.[2] The internal field which is set up depends very much on the shape of the medium and the *integral* (2) is *conditionally convergent*. For the center of a cube the field is exactly zero. Both these values, namely $4\pi P/3$ for the needle and zero for the cube are independent of the thickness of the needle and the size of the cube as long as we do not approach atomic dimensions. This size may, for instance, be infinitely great from which possibility we conclude that the essential characteristics of this group of cooperative actions is that the Lorentz field or some similar quantity is determined by a conditionally convergent sum or a conditionally convergent integral. It depends indeed on the shape in which we let our medium extend to infinite dimensions. The term infinite means here, infinite with respect to the size of the atoms, or infinite relative to the lattice constant of a crystal, etc.

The fields which are set up in ferromagnetic substances belong also to this group. Still other possibilities of self-perpetuating cooperative actions are imaginable, although they are not in common use in physics.

C. Other cooperative phenomena

I again give an example for illustration. It was first proposed by U. Dehlinger[3] in his theory of recrystallization. Dehlinger investigated the relative equilibrium of two parallel chains of atoms whose individual interactions are given. He shows that two dynamically stable configurations are possible. One is characterized by a constant and for both chains equal spacing of the atoms along the chain. There is another stable configuration, however, which is characterized by unequal spacings. In this arrangement there occur periodically slight accumulations, and slight scarcities, of atoms along the chain. Dehlinger calls them "Verhakungen." Under ordinary circumstances an individual "Verhakung" is unstable. A row of Verhakungen following one another in sufficiently short intervals, however, results in a dynamically stable configuration. The mutual stabilizing action of a row of Verhakungen is evidently a cooperative phenomenon which depends on the interaction of many atoms.

In two or three-dimensional arrays of atoms conditions are far more complex. From the fact that crystal lattices show many dynamically stable but thermally pseudostable configurations it must be inferred that arrangements similar to a row of Verhakungen are very frequent.

Another case of a cooperative phenomenon according to the quantum theory is related to the energy content of a solid body. This energy

[1] K. F. Herzfeld, Phys. Rev. **29**, 701 (1926).

[2] F. Zwicky, Phys. Rev. **38**, 1772 (1931).

[3] U. Dehlinger, Ann. d. Physik **2**, 780 (1929).

content depends on the so-called frequency spectrum of the body $\nu_1, \nu_2, \cdots \nu_n$. It has been proved that the high frequencies asymptotically tend towards the same distribution regardless of the shape of the body. The low frequencies (sound waves) however are essentially dependent on the external shape of the body. This makes the zero point energies $h\nu_{1/2}, h\nu_{2/2}, \cdots$ dependent also on the shape of the body and therefore introduces cooperative features into the thermal and caloric behavior of solids.

§3. Stationary Systems, "Static" and "Stationary" Thermodynamics

In thermodynamics we investigate the behavior of physical systems, that is the dependence of their pressure, energy, etc., on certain variable *static* parameters such as the density, the temperature, the external electric field, etc. We picture this behavior in phase diagrams, with the parameters as coordinates. The thermal equilibrium of a static system is determined by the condition that a certain function such as the total entropy or the total free energy, etc., is a maximum or minimum. Which one of these functions must be chosen depends on the type of variation which one investigates (adiabatic at constant volume, or isothermal at constant volume, etc.).

Static systems naturally are very special cases of physical systems which in general undergo changes in course of time. If we are looking for a *generalization of thermodynamics* it is logical to consider *stationary systems* as the next step towards the goal of formulating the laws of the macroscopic behavior of systems which change in time.

A stationary system is characterized by the fact that it depends not only on static parameters γ but in addition on at least one dynamical parameter γ' whose value is kept constant with respect to time. Examples of such systems are stationary flows of matter, of electricity, of radiation, or of heat, etc. The behavior of such a system may be geometrically represented in a phase diagram in which at least one dynamical parameter is used. It is immediately evident that in stationary systems the functions which assumed extreme values for static systems no longer possess this property.

Take for instance a long tube which is filled with sodium vapor. If the tube is in equilibrium with a great heat reservoir whose temperature T is constant the total free energy of the gas is a minimum. We may transform this static system into a stationary system by passing lengthwise through the tube ultraviolet radiation of constant intensity. The free energy of the system is then no longer a minimum. This is apparent from the fact that the new system possesses two different temperatures depending on whether we determine it by measuring the average kinetic energy of the gas atoms or the average specific energy of the radiation field. Gases which are distributed throughout the interstellar spaces form actually a system which is analogous to our example. Although the temperature of interstellar space is very low as far as the radiation field is concerned, the atoms nevertheless possess speeds corresponding to 10,000°C or more, because of the ionization and the ensuing recoils caused by the visible and ultraviolet light from the stars which sweeps the spaces.

The following new problem therefore suggests itself. Which functions Γ take the place of the entropy, the free energy, etc., in the case of stationary systems? I shall not here go into detail about this problem. A little consideration, however, shows that the Γ's must be of the form

$$\Gamma = \text{function of } [\gamma, \gamma', B, (\partial/\partial S_i)(\gamma, \gamma')]. \quad (8)$$

Here γ and γ' are the static and the stationary parameters, respectively. Essentially new is the dependence of Γ on the boundary conditions B and on the differential coefficients of the intensive parameters with respect to the spatial coordinates S_i. For our considerations the occurrence of B is important. This means that in stationary systems we necessarily are confronted with *cooperative phenomena*. This conclusion is not only important for the behavior of actually stationary systems but it also has serious consequences with regard to many important characteristics of actually static systems which we find in nature or produce in the laboratory. This peculiar conclusion is related to the existence of thermally *pseudostable systems*. For more details I refer to the next sections.

An interesting stationary system was once

treated by W. Nernst.[4] He investigated the dissociation equilibrium of a gas in a stationary flow of heat. The relative concentrations of the molecules and the particles into which they dissociate not only depend on the temperature T and the pressure p at a given point but also on grad T. This is easily understood because of the diffusion through the boundary of two adjacent volume elements which are held at two different temperatures by the heat flow.

It may not be superfluous to add that there are systems of *apparently stationary* character which nevertheless are governed by the same laws as static systems. This happens when the stationary character of the system is only due to a transformation of coordinates.

For the extension of thermodynamics which I have suggested in the above I propose the name *stationary thermodynamics* in contradistinction to the usual older discipline which might more specifically be called *static thermodynamics*. Whether and how the characteristic canonical functions Γ can generally be determined is a problem for further investigations. Two methods suggest themselves. One is to apply static thermodynamics to differential parts of a stationary system. The second method consists in using statistical methods in investigating certain characteristic statistical games or models.[5] If general methods can be found they will naturally be of great value as stationary systems are very frequent and of great importance. I mention among others: (A) stationary flows of liquids and the problem of turbulence; (B) stationary flows of heat and of electricity; (C) flows of liquids such as blood or saps in plants. An important problem here is how chemical reactions take place on cell walls subjected to stationary flows.

§4. The Problem of the Solid State

Some of the most important applications of our previous considerations lie in the vast field which may shortly be called the physics of solids or more specifically the physics of crystals.

I shall first discuss a few general characteristics of crystals and I shall try to show that cooperative actions between many particles are mainly responsible for the existence of a crystalline state. I then shall describe how such cooperative actions in general necessitate the formation of a *secondary structure of crystals*.

One of the most surprising characteristics of crystals is the existence of an extremely well-defined temperature of the melting point. Indeed, most crystals, if held at constant pressure, melt within a very small range of temperature, the range being usually too small for an actual determination of its width. This fact has been known for a long time, which however does not render it any more comprehensible. As I have explained already in another place[6] the difficulty lies in the following circumstance. If the formation of a crystal lattice were due to the interaction of each of its atoms with a limited number of neighboring atoms then melting, according to statistical mechanics, should be a phenomenon similar to the dissociation of polyatomic molecules containing a corresponding number of atoms. Melting similar to dissociation of polyatomic molecules at constant pressure then would extend over quite a considerable range of temperature. A sharp melting point is comprehensible only if cooperative phenomena between a great number of atoms are responsible for the existence of crystals.

A second fact which points very strongly towards the existence of cooperative phenomena in solids is the surprisingly accurate line-up of crystalline planes over macroscopic distances. Calcite planes for instance are lined up to a few seconds of arc over a distance of one centimeter. It is very difficult to understand this fact on the basis of individual interactions, which, as we know, are greatly disturbed by temperature agitation. It is still harder to understand why even quite appreciable layers of foreign atoms do not disturb the line-up.

In the third place the enormous influence of a few absorbed foreign atoms suggests for its explanation the existence of cooperative phenomena. The recrystallization through grain boundaries which are occupied by many layers of contaminating atoms might be mentioned in this connection also.

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[4] W. Nernst, *Boltzmann Festschrift*, p. 904 (1904).

[5] P. and T. Ehrenfest, Encyklopädie d. math. Wissenschaften IV, 2, No. 6, p. 82.

[6] F. Zwicky, Proc. Nat. Acad. Sci. 17, 524 (1931).

Fourthly, volume effects are known to exist even for crystal grains of macroscopic size.[7]

The phenomena discussed in the above necessitate the existence of cooperative phenomena in crystals. Which particular cooperative phenomenon is responsible for a particular kind of crystal must be decided by a special theoretical or experimental investigation.

As far as the geometrical arrangement of atoms in a crystal is concerned we are now confronted with the following situation. The *primary structure* will essentially be determined by the type of *individual* interaction between neighboring atoms. It may for instance be cubic. On top of this we must consider the action of a certain cooperative phenomenon which may have a symmetry character other than the primary structure, say tetragonal. The cooperative phenomenon will therefore have a tendency to distort the primary structure, this effect being in general a very slight one. If now our crystal had always the shape of a long thin needle its structure would be homogeneous and slightly tetragonal. If, however, the crystal is of any other shape the surfaces will disturb the formation of a uniformly tetragonal structure. At the surfaces the cooperative phenomenon which is characteristic for one crystal will indeed produce results different from those in the interior of the crystal. It would then follow that different effects would be obtained for different shapes of crystals. A crystal also would not possess any equation of state. It can however be shown in special cases that through the formation of a secondary structure a compromise is reached which reconciles the antagonistic tendencies of the individual and the cooperative actions. In the above example this means that the crystal is subdivided into equal regions or blocks whose tetragonal axes alternate in a periodic fashion between the directions $[\pm 1, \pm 1, \pm 1]$. This case is for instance realized if a self-perpetuating electric or magnetic polarization may be set up along any of the three principal directions in a cubical crystal. For details I must refer the reader to a discussion which I have given elsewhere.[8]

Generalizing the above considerations we may state that the antagonistic tendencies of the individual and the cooperative actions between the elementary building stones of a crystal are likely to lead to the formation of a secondary structure, provided that the symmetry characters of the two phenomena are different. If the symmetry characters happen to be the same it is conceivable that ideal crystal lattices may be formed. This might be true for some diamonds. My only support for this statement is that diamond has a slipping strength which seems to be of the order which one expects for an ideal lattice.

Our general conclusion may be stated schematically as follows:

Individual actions ——— primary structure

Cooperative actions ——— secondary structure.

The cooperative actions at the same time account for the fact that crystals exist at all.

In regard to the individual interactions between atoms it should be remarked that they cause, statistically speaking, the existence of a primary structure even in the liquid state. This view is supported by the facts which have recently been obtained by the x-ray investigations of liquids.

Finally mention must be made of cooperative phenomena which act during the growth of crystals. In the simplest case of the uniform growth of a crystal in one direction only we are dealing with such a stationary system. The essential characteristic of such a system is that the heat of fusion which is liberated on solidification is carried off in the form of a stationary flow. This flow necessitates the existence of a temperature gradient. This gradient for ordinary rates of growth is great enough to produce a plastic deformation of the crystal in *statu nascendi*, as I have shown in another place.[7] If the crystal is not annealed during the cooling process it will remain in a partially deformed state. The resulting crystal will be thermodynamically pseudostable. This pseudostable configuration therefore is the result of the cooperative phenomenon which is caused by the stationary character of the process of growth. There exist many other phenomena of this type.

§5. Remarks on Ferromagnetism

Ferromagnetism from all we know must be regarded as a typical cooperative phenomenon

[7] F. Zwicky, Phys. Rev. **40**, 63 (1932).

[8] F. Zwicky, Phys. Rev. **38**, 1772 (1931).

whose existence is due to the interaction of a great number of elementary particles. Ferromagnetism provides excellent illustrations for some of the contentions of this paper.

Let us discuss some of the characteristics of the simple theory of ferromagnetism due to P. Weiss. He assumes that in a ferromagnetic substance there are N magnetic dipoles μ per cm^3 which may freely rotate. If the medium is isotropic and infinitely extended (without any boundaries) the dipoles are acted upon by a total field

$$H_t = H_e + H_m \tag{9}$$

where H_e denotes the applied field and H_m the so-called molecular field. If the dipoles were of electric origin or if we deal with a gas such as NO whose molecules possess magnetic moments, then

$$H_m = 4\pi I/3, \tag{10}$$

where I is the intensity of the electric or the magnetic polarization respectively. Weiss showed however that in order to obtain an adequate theory of ferromagnetism one must put

$$H_m = \alpha I, \tag{11}$$

where α is of the order of 10,000. Quantum mechanics recently has furnished a rational explanation of these high values of α.

Under certain conditions (N large and T small) the above equations result in a permanent magnetization of our substance. If $\bar{\mu}$ is the average magnetic moment per particle in the direction of $H_t = H_m$, assuming $H_e = 0$, then

$$\bar{\mu}/\mu = \operatorname{Coth} x - 1/x$$

$$x = \mu H_m/KT \quad \text{and} \quad I = N\bar{\mu}, \tag{12}$$

where K is Boltzmann's constant. For $H_e = 0$ and T sufficiently low we have $\bar{\mu} \neq 0$. This resulting permanent magnetization is a typically cooperative phenomenon as the existence of the molecular field $H_m = \alpha N\bar{\mu}$ is caused by a macroscopic amount of matter containing a great number of dipoles. As we have claimed for such phenomena it has a sharp *melting point* at

$$T = \theta = \alpha N\mu^2/3K. \tag{13}$$

This melting point is usually called the Curie point. Near $T = \theta$ we may expand, as x is small, and we obtain

$$\bar{\mu}^2 = -45(KT/\alpha N\mu)^3/\mu + 15(KT/N\alpha\mu)^2$$

$$\bar{\mu}^2/\mu^2 = 5(T/\Theta)^2(\Theta - T)/3\Theta, \tag{14}$$

which is a parabola for $T \sim \Theta$. This results in $\bar{\mu} = 0$ for $T = \Theta$. It is

$$d\bar{\mu}^2/dT = -5\mu^2/3\Theta = -5K/\alpha N$$

or as $\bar{\mu}(\Theta) = 0$ we have $d\bar{\mu}/dT = \infty$ for $T = \Theta$. This means that the melting point of ferromagnetism (its disappearance with T) is infinitely sharp. This is in accordance with our contention that the cooperation of many particles is responsible for the existence of sharp melting points. If a finite system of dipoles were considered the sharpness of the melting point would be decreased because of surface effects and for only a few dipoles cooperating the melting would take on the character of a dissociation spread over a wide range of temperatures.

It goes without saying that ferromagnetism exhibits all the other characteristics of a typically cooperative effect. It indeed implies a lineup of magnetic moments over macroscopic distances. It depends very much on small amounts of impurities present. It is structure-sensitive and it shows volume effects inasmuch as particles of colloidal size do not have the same magnetic characteristics as bigger particles.

Both from the Weiss theory and from the more modern quantum mechanical explanation one would expect in the first approximation a uniform line-up of the magnetic moments in one of the directions of easiest magnetization of a ferromagnetic crystal. This means that such a crystal for $H_e = 0$ should exhibit a permanent magnetic moment different from zero. In reality this is not the case as a single crystal as a whole is unmagnetic. From the caloric behavior, that is, the specific heat, it is known that the permanent magnetization exists. This forces us to assume a subdivision of the crystals into magnetically saturated regions whose moments however balance out over the whole crystal. The reason for this probably lies in the following. If the crystal were magnetized as a whole it would not possess any equation of state because the demagnetizing effect of the surface would depend on the macroscopic shape of the crystal. An energy loss cor-

responds to this as the demagnetizing field is directed oppositely to H_m. This loss can be avoided if the crystal is subdivided into bundles of long needles which are alternately magnetized in opposite directions. Such an arrangement has a demagnetizing field equal to zero. The theory of course is confronted with the task of proving that the loss of energy along the surfaces of the oppositely magnetized needles is less than the loss corresponding to the demagnetizing field of a uniformly magnetized crystal. Experimentally, however, this seems to be established. Assuming this to be correct the elementary regions of uniform magnetization can be found by the procedure suggested previously by Dr. H. M. Evjen and myself. This method suggests the following subdivisions or *magnetic secondary structures* for Co, Ni and Fe.

Cobalt is hexagonal with the direction of easiest magnetization along the hexagonal axis. The simplest magnetic secondary structure would be obtained if needles parallel to the hexagonal axis and of triangular cross section are alternately magnetized in opposite directions. In the basal plane we would have an arrangement as shown in Fig. 1. Shading means magnetization

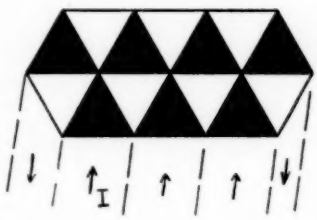

FIG. 1. Basal plane of cobalt.[9]

upwards. The other needles are magnetized downwards. If needles of hexagonal cross section are used a symmetrical arrangement can only be obtained if three states of magnetization are admitted, upward (+), downward (−), and zero (0) which would give the picture (2). The two arrangements would be different in regard to the caloric behavior of the crystals. If therefore from the caloric behavior complete saturation of the crystal can be deduced an arrangement of the type of Fig. 1 must be chosen.

It is well known that a type of magnetic secondary structure in Co has been found by F. Bitter[10] who observed that F_2O_3 colloidal particles will settle in regular arrays on Co crystals. The particles settled in an array similar to a dense star field on the basal plane and in straight lines in a plane parallel to the hexagonal axis. This is in accordance with our suggestion of needles parallel to the hexagonal axis being alternately magnetized in opposite directions. The thickness of the needles is experimentally of the order 10μ.

In nickel which is a cubic crystal the direction of easiest magnetization is along the body di-

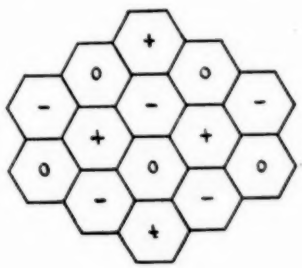

FIG. 2.

agonal [111] of the cube. An adequate secondary structure is obtained by magnetizing alternately needles with a square cross section. The needles must be parallel to one of the three principal directions of the cube and the largest uniformly magnetized regions will be cubes with the resultant magnetic moment in the direction of one of its body diagonals.

F. Bitter has not obtained any patterns of the settled colloidal particles in this case for a zero external field. This means that the secondary structure is characterized by a lattice constant which is too small to be resolved by his method. If a field is applied, however, the particles settle in equidistant straight lines which are approximately normal to the applied field. This might be interpreted in the following way which is in accordance with our previous considerations. One would expect off-hand that on application of an external field H_e the whole magnetic secondary

[9] Notice that the two types of triangles are mirror images. In which way this fact provides a very simple illustration for the existence of a secondary structure in many crystals will be discussed in one of my next publications.

[10] F. Bitter, Phys. Rev. **38**, 1903 (1931) and **41**, 507 (1932).

structure would disappear and that the crystal would appear uniformly magnetized along that diagonal of the elementary crystallographic cube which is nearest to the direction of H_e. This, however, would result in a maximum demagnetizing effect of the surface. It seems therefore energetically more advantageous to make use of more than one, and, may be, of all four space diagonals choosing on every one, of course, that direction which is nearer to the direction of the external field. This would result in an alignment of the magnetic vectors which in a two-dimensional representation is schematically shown in Fig. 3. Although the magnetic stray fields are

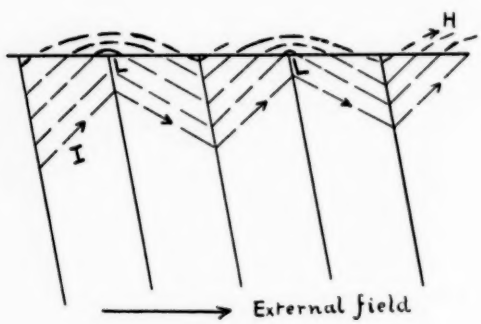

FIG. 3. Nickel in a magnetic field.

present all over the surface the colloidal particles would be drawn in only at places where the field is strongly inhomogeneous and would settle along the lines L, which agrees qualitatively with F. Bitter's findings. An experimental investigation is under way in this Institute to measure out the distribution of the magnetic stray fields on the surface directly. From this investigation much more detailed information about the phenomenon in question may be hoped for.

In iron the direction of easiest magnetization is along the principal axes of the elementary cube, that is, along one of the axes $[\pm 1, 0, 0]$, $[0, \pm 1, 0]$ or $[0, 0, \pm 1]$. The elementary cells of the magnetic secondary structure therefore must be alternately magnetized along one of these six directions. Two relatively simple solutions suggest themselves. The elementary cells of the first solution are regular octahedra and tetrahedra, whose four essentially different faces are respectively normal to the space diagonals of the elementary cube of the primary structure. The second solution uses regular rhombic dodecahedra with faces which are respectively parallel to the twelve planes of the type (110). This latter solution cannot be built up by an interpenetration of sets of infinite needles. In both solutions the elementary cells of the secondary structure are alternately magnetized in the principal directions [1, 0, 0], etc. As iron single crystals do not seem to possess any crystallographically distinguished slip planes the solution using rhombic dodecahedra seems to be the more adequate. However, further experimental investigations will be necessary to solve the problems related to the geometry of the magnetic secondary structure of ferromagnetic crystals.

Just as in the case of nickel the characteristic spacing of the magnetic secondary structure in iron is too small to be resolved by Bitter's method. With an applied external field however one obtains striations similar to the case of nickel.

Bitter's experiments prove without any doubt the existence and intrinsic importance of cooperative phenomena. As the striations which he obtains may be shifted at will relative to the boundaries of the crystal it is impossible to make imperfections (or mosaic structure) responsible for the phenomena in question. The effects discovered by him therefore prove conclusively the possibility and the actual existence of secondary structures as I have postulated them several years ago.

This short sketch may suffice for the present to make clear the vital importance of cooperative phenomena for a deeper understanding of the nature of the crystalline state. As mentioned before, cooperative actions between many particles are not confined to crystals. They play an important part in other systems and are probably most essential for the possibility of living organisms.

Electronic Structures of Polyatomic Molecules and Valence. IV. Electronic States, Quantum Theory of the Double Bond

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The possible types of electronic states of polyatomic molecules (assuming fixed nuclei and neglecting spin fine structure) are discussed and tabulated (Table I) with the help of simple group theory methods, applying results of Bethe and Wigner. A notation for electronic states (ψ's) and molecular orbitals (ϕ's) for molecules having any type of symmetry to be found among the 32 crystal classes, is adopted; this is essentially the same as that used by Placzek for designating the vibrational states of molecules. It is shown how the possible ψ's corresponding to any given electron configuration (set of ϕ's) can be determined for any type of symmetry; for the more complicated cases, the results are tabulated (Table V). It is shown how all the *selection rules* for transitions between electronic states of molecules can be easily determined. Limitations resulting here from the application of the Franck-Condon principle are discussed. Extending work of Bethe, tables are given (Tables II–IV) showing how the various types of electronic states of atoms and of diatomic and polyatomic molecules (S, P, Σ^+, ΔA, etc.) go over into various other types of states if the symmetry of the original system is decreased. Examples are given showing how electronic wave functions (ψ's) of molecules can be constructed which conform to the possible types (Table I) allowed by the symmetry of the nuclear skeleton, and which at the same time, with Slater's method, are antisymmetrical in the electrons (cf. section 2 and Eqs. (9–12)). It is shown that for molecules having all their electrons in closed shells or electron-pair bonds, zeroth approximation ψ's which conform to the identical representation of the molecule's symmetry group (analogous to ^1S of atoms and $^1\Sigma^+$ or $^1\Sigma_g^+$ of diatomic molecules) can be built up either by using electron-pair bonds or by using molecular orbitals. The approximate construction of molecular orbitals as linear combinations of atomic orbitals, in such a way that they conform to the types allowed by the symmetry of the molecule, is discussed and illustrated (cf. Eqs. (3, 8)). Several statements made in a previous paper (III) of this series, on the quantum theory of the double bond, are here justified by the methods mentioned above, thereby also providing examples of the application of the latter. Some additional details concerning the nature of the double bond are given. Finally, it is shown that the model of the double bond given in III should according to the theory be altered somewhat for the perp. form of the molecule, in a way which offers the possibility of improved agreement with experiment.

INTRODUCTION

1. Symmetry of electronic wave functions

In I, II and III of this series[1] the use of molecular orbitals for shared electrons in describing and interpreting the electronic states of polyatomic molecules has been discussed and illustrated.[2] Discussion of further examples will be prefaced by some general considerations.—Through an oversight, the writer failed to mention in II that Hückel also[3] has been following a similar program in his work on the structure of the benzene ring, its derivatives, and certain other organic compounds. In this connection Hückel also has made a comparison of the methods of molecular orbitals and of electron-pair bonds.

For a molecule with fixed nuclei, the complete electronic wave function ψ is restricted to one of certain types which depend on the symmetry of the nuclear skeleton. In the language of group theory, ψ must conform to an irreducible representation of the symmetry group of the corresponding Schrödinger equation,—which contains a potential energy whose symmetry is that of the nuclear skeleton. Or more briefly, one may say that every ψ must belong to an irreducible

* Fellow of the John Simon Guggenheim Memorial Foundation.

[1] R. S. Mulliken, Phys. Rev. **40**, 55; **41**, 49, 751 (1932). Hereafter designated as I, II, III.

[2] Cf. II, also J. C. Slater, Phys. Rev. **41**, 255 (1932), for a comparison of the method of electron-pair bonds with that of molecular orbitals.

[3] E. Hückel, Zeits. f. Physik **70**, 204; **72**, 310 (1931); **76**, 628 (1932). Also it should be mentioned that the interpretation of the structure of C_6H_6 attributed in II (p. 56) exclusively to Hund had already appeared in Hückel's paper on this molecule.

representation of the symmetry group of the nuclear skeleton. Corresponding statements apply to every molecular orbital φ. In nature ψ is of course further restricted, in accordance with the Pauli principle, to forms antisymmetrical in the electrons.

In general a knowledge, for any nuclear configuration, of the different irreducible representations of its symmetry group, since these determine the forms or types to which ψ and the φ's may belong, is important in determining the number, spacing, and degree of degeneracy of molecular electronic states, and the selection rules for transitions between them, also for determining the possible states of the dissociation products of a molecule.

Like the electronic φ's and ψ's, the possible states of vibration of a (rotationless) molecule also conform to the irreducible representations of the symmetry group of the molecular skeleton (in its equilibrium or in some more symmetrical configuration).[4, 5] Finally, the *total* electronic $\times$vibrational *state*, excluding rotation, must belong to such a representation. This is strictly true even when the electronic and vibrational parts of the wave function cannot be even approximately separated.

The process of finding the irreducible representations for any given type of molecular symmetry is accomplished in an easy and instructive way (cf. section 4), by using a little group theory. The problem has already been solved, for all or most of the kinds of symmetry likely to occur in actual molecules, by Bethe[6] and Wigner.[4] The results have been applied by Wigner and by Placzek[5] to the case of nuclear vibrations, of importance especially for Raman and infrared spectra.

An important secondary problem is that of notation. It has seemed best here to adopt for classifying electronic φ's and ψ's (Table I below) essentially the same notation Placzek has used for describing vibrational states. The same notation could well be used also for the electronic φ's and ψ's of atoms in crystals (Bethe's problem[6]), and the same or a similar notation for describing the electronic$\times$vibrational states of molecules. Placzek's notation has marked advantages over the Bethe notation used in I–III of this series, in being more descriptive.

These problems will be taken up again in section 3. In section 2 the matter of building up good approximate ψ's which are antisymmetrical in the electrons will be considered.

In classifying electronic states of polyatomic molecules, complications often arise because of the existence of more than one fairly stable arrangement of the same set of nuclei. Such different arrangements as are chemically stable (chemical isomers) can when in their normal states most conveniently be treated as distinct individuals. In excited states of such molecules, the relative stabilities of different arrangements are in general altered. It may then often be advisable to regard a variety of nuclear arrangements as belonging to a single molecular species. This is of course always necessary to a greater or less degree when one considers excited molecules in which strong vibrations or internal rotations are occurring.

Even for unexcited molecules belonging to a single chemical species it is not always true that there is just a single very stable type of nuclear configuration. In C_2H_6, for example, only very weak forces[7] oppose a relative rotation of the two CH_3 groups around the C–C axis. Hence in discussing the electronic structure of C_2H_6, it is perhaps best to assume only such symmetry as is common to the various forms differing by arbitrary rotations of this kind. Another less extreme example is found in NH_3, where a plane

[4] E. Wigner, Göttinger Nachr., Math.-Phys. Klasse, p. 133 (1930). Wigner extended Bethe's results (see reference 6) to include the symmetry groups of all the 32 crystal classes.

[5] G. Placzek, article on Raman and infrared spectra, to appear soon in *Marx's Handbuch der Radiologie*. The writer is indebted to Dr. Placzek for the use of his tables before publication and for valuable discussions, also for calling his attention to reference 4. Placzek gives his tables without direct use of group theory, but they are essentially the same as the group theory results (cf. Table I below).

[6] H. Bethe (Ann. d. Physik [5], **3**, 133 (1929)) used group theory in determining the irreducible representations to which the ψ and φ's of an atom may belong when in a field of force corresponding to that produced by its neighbors in a crystal. The writer is greatly indebted to Professor J. H. Van Vleck for calling his attention to the applicability of Bethe's results to molecular electron wave functions.

[7] Cf. H. Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

form is nearly as stable as the pyramidal equilibrium forms.

2. Use of atomic and molecular orbitals to build up ψ

The complete electronic wave function ψ of a molecule can be conveniently approximated by an antisymmetrical linear combination of products of atomic or molecular one-electron wave functions, each a product of an orbital factor φ and a spin factor σ. This can be done in various ways. In any case one may start with a determinant form as follows (N is a normalizing factor):

$$U = N \begin{vmatrix} \varphi_1\sigma_1(1) & \varphi_1\sigma_1(2) & \cdots \\ \varphi_2\sigma_2(1) & \varphi_2\sigma_2(2) & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix} \qquad (1)$$

This is antisymmetrical in the electrons 1, 2, 3, . . . Using a set of such U's as unperturbed functions, one can obtain the desired wave functions ψ as linear combinations of them (*general method* of Slater[8, 9]). In so doing, one includes in any linear combination only such U's as have the same M_S (resultant spin magnetic quantum number).[8] [In the case of atoms, one includes only such U's as are alike also in M_L.]

Various cases may arise. In general one has in the unperturbed system (no interactions between electrons) several U's of equal energy corresponding to a given set of φ's but various arrangements of σ's giving the same M_S (spin degeneracy), and to a variety of sets of equivalent φ's for any given spin arrangement (orbital degeneracy). In some cases (e.g., an atom or molecule built of closed shells of atomic or molecular orbitals respectively), there is no such degeneracy and a single U suffices.—In the case of any molecule, every linear combination of U's must be so chosen as to conform to an irreducible representation of the molecule's symmetry group (cf. section 1).

To get the best practical approximation (Slater's most general practical method,[10] (see also reference 9, page 1111)) one includes not only such U's as are really degenerate in the unperturbed system, but also other U's of equal M_S, etc., whose energies lie in the same neighborhood. It should be noted that the U's belonging to a really degenerate set always belong to a definite electron configuration, i.e., to a definite set of φ's (counting degenerate φ's as belonging to a single type), distributed, if there is more than one atom, with a definite set of φ's for each atom. The use of an approximation built up only from a really degenerate set of U's may therefore appropriately be referred to as the *method of the pure electron configuration*.

As applied to molecules, the method of the pure electron configuration may be specialized or approximated in various ways. The present *method of molecular orbitals* is a special form in which, following Lennard-Jones, atomic φ's (orbitals) are used for inner or unshared electrons (usually in atomic closed shells), molecular φ's for outer, shared or valence, electrons. The form used by Slater[8, 9] which for convenience will be called the "*method of atomic orbitals*," is one in which atomic φ's exclusively are used. A special case of the method of atomic orbitals, sometimes identical with it but in general representing a simpler but cruder approximation, is the Slater-Pauling *method of electron-pair bonds*. This last is applicable only to chemically saturated molecules in their normal states, i.e., to a restricted but particularly important class of molecular states.

Following a method first used by Bloch for metals[11] and later used by Hückel, Hund, and others, molecular orbitals will as a matter of convenience usually be approximated here by linear combinations of atomic orbitals, although eventually we may hope to obtain forms which are better approximations. When atomic orbitals are used in constructing molecular orbitals, the resulting ψ is in the final analysis expressed entirely in terms of atomic orbitals, but is nevertheless not in general identical with that obtained with the "method of atomic orbitals" as defined above. For excited states, to be sure, the approximate ψ's given by the two methods are very often identical: examples, $^3\Sigma_u^+$ and $^1\Sigma_u^+$ states of H_2 built up, respectively, in the atomic orbital method, from 2 H($1s$) and from $H^+ + H^-(1s^2)$. For saturated molecules in their normal states, however, and whenever there is

[8] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[9] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[10] For examples of this case cf. E. U. Condon, Phys. Rev. **36**, 1121 (1930), and other papers.

[11] F. Bloch, Zeits. f. Physik **52**, 555 (1928).

at least one pair of electrons which form a valence bond, the two methods are never identical. Nevertheless the approximations given by the two methods can of course always be made identical if we generalize (and complicate) each, dropping their common "pure electron configuration" limitation, and form linear combinations with U's belonging to other configurations. It is still true, however, that the point of view and method of approach are different in the method of molecular orbitals than in that of atomic orbitals or of electron-pair bonds. Slater[2] has pointed out the usefulness of considering problems from both points of view.

In building up ψ's for complicated molecules according to the present method, it will often be useful to proceed in two or more stages, first assigning electron configurations composed of (atomic and) molecular orbitals for separate parts of the molecule (*radicals*), then combining these. Two courses are then open for the construction of ψ for the complete molecule. (1) One may proceed in accordance with the method of molecular orbitals, using molecular orbitals of the total molecule for those electrons which may reasonably be considered as shared by the two or more radicals, but keeping *radical orbitals* for those electrons which are shared within, but not between radicals (and of course using atomic orbitals for electrons which belong to particular atoms and are not shared at all). (2) Or one may proceed in analogy with the method of atomic orbitals, building up the final ψ entirely from orbitals of the various radicals (and atomic orbitals for the completely unshared electrons). One may form electron-pair bonds from radical orbitals if the latter are known to give bonding.

Good examples of molecules which can be built up out of radicals are C_2H_4 and its derivatives. Both procedures (1) and (2), but especially (1), will be used in section 8*d* below for building up ψ's of C_2H_4 using CH_2 orbitals. A symmetrical molecule like C_2H_4 when treated in this way is analogous to a homopolar diatomic molecule. In plane C_2H_4 the analogy is close, in perp. C_2H_4 less so in some respects. In practice (cf. the $[z]$ and $[x]$ orbitals of CH_2 used in forming C_2H_4) those radical orbitals which act as valence orbitals of a radical, forming bonding electron pairs in the complete molecule, are really often to a fairly good approximation just atomic orbitals of certain atoms between which binding chiefly occurs. Cf. the $[z]$ and $[x]$ orbitals of CH_2 used in forming the C=C double bond in C_2H_4; these are not far different from C atom orbitals. Hence one need not fear that the use of the method of molecular orbitals in complex molecules necessarily means using orbitals which are spread over a large number of atoms. Even in large molecules, it will be found that one arrives at molecular orbitals which usually fade out after bridging the gap between any atom and one or more of its immediate neighbors. Especially in hydrides, however, many details of chemistry may prove to be better understandable by admitting molecular orbitals which do extend with appreciable density somewhat farther than this (cf. section 8*e* for an example; a still better example is probably B_2H_6).

2a. Method of electron-pair bonds. It will be instructive first to say something about the electron-pair bond method. In this, the ψ of a molecule with definite bonds is approximated[9] by a linear combination of the type

$$\psi = N\begin{vmatrix} \varphi_1\alpha(1) & \varphi_1\alpha(2) & \cdots \\ \varphi_2\beta(1) & \varphi_2\beta(2) & \cdots \\ \varphi_3\alpha(1) & \varphi_3\alpha(2) & \cdots \\ \varphi_4\beta(1) & \varphi_4\beta(2) & \cdots \\ \text{etc.} & \cdots & \cdots \end{vmatrix} - N\begin{vmatrix} \varphi_1\beta & \cdots \\ \varphi_2\alpha & \cdots \\ \varphi_3\alpha & \cdots \\ \varphi_4\beta & \cdots \\ \cdots & \cdots \end{vmatrix} + N\begin{vmatrix} \varphi_1\beta & \cdots \\ \varphi_2\alpha & \cdots \\ \varphi_3\beta & \cdots \\ \varphi_4\alpha & \cdots \\ \cdots & \cdots \end{vmatrix} - N\begin{vmatrix} \varphi_1\alpha & \cdots \\ \varphi_2\beta & \cdots \\ \varphi_3\beta & \cdots \\ \varphi_4\alpha & \cdots \\ \cdots & \cdots \end{vmatrix} + \text{etc.} \qquad (2)$$

The number of U's in this expression depends on the number of bonds. For H_2, with one bond, there are just two U's, each in the form of a determinant with two rows and columns, and with φ_1 and φ_2 denoting H atom 1*s* orbitals, one for atom A, the other for atom B.[9] For a molecule He_2, with no bonds, there would be only one U, with $\varphi_1 = \varphi_2$, and $\varphi_3 = \varphi_4$, φ_1 and φ_3 referring to a a 1*s* orbital on He atom A or B respectively.

For H_2O, with two bonds and approximately a 90° angle between them, ψ would consist of four U's, with φ_1 and φ_3 representing, say, a $2p_y$

and a $2p_z$ oxygen orbital, φ_2 and φ_4 representing $1s$ orbitals of the two hydrogen atoms; each of the four determinants would also contain terms corresponding to six more electrons and to wave functions $\varphi_4\alpha$, $\varphi_5\beta$, $\varphi_6\alpha$, $\varphi_6\beta$, $\varphi_7\alpha$, and $\varphi_7\beta$, where φ_5, φ_6, φ_7 refer to oxygen $1s$, $2s$, and $2p_x$ orbitals, which do not form bonds. Similarly the Slater-Pauling model of NH_3 is approximated by using three bonds between nitrogen p_x, p_y, and p_z and hydrogen $1s$ orbitals. In every case, orbitals which are to be used in forming bonds belong to different atoms and appear with opposite spins (α and β) on the two atoms (cf. reference 9, top page 1128, for details).

In dealing with compounds of N, O, F, and their homologues, Slater and Pauling assume as a good approximation that it is only the p electrons which form the bonds. They generally use as suitable zeroth approximations atomic orbitals of the types p_x, p_y, and p_z (i.e., $f(r)$ $\sin\theta\cos\varphi$, $f(r)\sin\theta\sin\varphi$, and $f(r)\cos\theta$). For the univalent atoms such as H, Na, they, of course, use s orbitals.

For the carbon atom, Slater and Pauling use "tetrahedral" orbitals. These comprise four energetically and geometrically equivalent linear combinations[12] of $2s$ and $2p$ orbitals pointing toward the corners of a tetrahedron. Strongest binding of other atoms is then obtained if the latter are at the corners of a tetrahedron. For CH_4, the expression for ψ written down according to Eq. (2) contains sixteen U's. Each U has $\varphi_1=\varphi_2=$carbon $1s$, $\varphi_3=\frac{1}{2}(s+p_x+p_y+p_z)$ of carbon, $\varphi_4=$the H $1s$ which overlaps φ_3, and so on to φ_{10}.

For any saturated molecule (unshared electrons all in atomic closed shells and shared electrons all in electron-pair bonds), ψ, as well as every one of the U's, if chosen as in Eq. (2) and with atomic orbitals properly adapted to the symmetry of the molecule, can be shown to belong always to the "identical representation" of the symmetry group of the molecule, with zero spin (^1A or $^1A_1$ or $^1A_{1g}$, etc.).

The proof is as follows (cf. sections 3, 4 and Table I for necessary group theory and discussion of symmetry types). First we note that for a saturated molecule, every properly-constructed approximate U and ψ of the type found in Eq. (2) must contain for every atom one wave function for every bond which the atom forms, and for any atom which forms more than one bond of the same kind, the zeroth approximation wave functions used for these bonds must be equivalent, i.e., must transform one into another under the operations of the symmetry group (cf. e.g., the Pauling-Slater tetrahedral orbitals). [If this last condition is not met, one must in general use a linear combination of several expressions of the form of ψ in Eq. (2) in order to get a final ψ which is a representation of the symmetry group. For molecules which are not saturated, it is always necessary to form such linear combinations, by using the general form of the method of atomic orbitals, since the more special method of electron-pair bonds is not applicable.] If these conditions are fulfilled, then the effect on any U of any symmetry operation belonging to the symmetry group defined by the nuclear configuration is readily seen to be merely to permute some of the rows in its determinant (Eq. (1)), but never to eliminate any row nor to introduce any new kind of row. Every symmetry operation either leaves all φ's unchanged, or replaces some of them by other equivalent ones; it does not affect the spins (α, β). The totality of permutations produced by any operation can always be expressed in terms of a certain number of specified transpositions (exchanges) of rows. Now the value of a determinant is multiplied by -1 if an odd number, by $+1$ if an even number of transpositions of its rows is made. One now sees (1): for the totality of electrons which are in atomic closed shells, every symmetry operation produces an even number of transpositions of rows, simply because there is an even number of wave functions in the closed shells of each atom; equivalent atoms of course have equivalent closed shells; (2): the wave functions of any two electrons (one on each of two atoms) which form a bond undergo parallel transformations under any symmetry operation, and from this it is easily seen to follow that the total number of transpositions of rows resulting from the action of any symmetry operation on the bonding electron wave functions is even. Hence for a saturated molecule whose ψ is constructed as above specified, the total number of

[12] L. Pauling, J. Am. Chem. Soc. **53**, 1378 (1931).

transpositions produced in each U by any symmetry operation is even, so that each U, and ψ, is multiplied by $+1$ for every operation of its symmetry group. This behavior is that which characterizes the *identical representation* of any symmetry group; this representation has the same symmetry as the nuclear skeleton itself.

It should be noted that the result just proved holds even if the actual molecule, e.g., H_2O, does not have the ideal valence angles (90°, etc.) of Pauling and Slater, provided only that the axes for the atomic orbitals used are chosen with proper regard for the actual symmetry of the molecule. The reader can readily verify the correctness of the result of the last paragraph for the cases of H_2, He_2, H_2O, NH_3, CH_4, whose ψ's were given above, by testing what happens to each U or ψ when subjected to each operation (cf. Table I) of the appropriate symmetry group.

2b. Method of molecular orbitals. We shall assume that the symmetry of the molecule is known, empirically or perhaps from the Pauling-Slater electron-pair bond rules. In order to obtain ψ's, one inserts the proper orbitals, some atomic and molecular, into Eq. (1). A suitable linear combination of the resulting U's formed in exactly the same way as in the case[8] of an atom.

The main problem is usually that of finding suitable molecular orbitals. In the first place, these must always be representations of the symmetry group defined by the arrangement of the nuclei. For molecules in their normal states, one must furthermore usually select only *bonding* molecular orbitals. These are characterized by giving a relatively high probability density between the nuclei which they bind together. The fulfillment of this condition is assured, if one constructs the molecular orbitals approximately by taking linear combinations of atomic orbitals, by using only combinations which add between nuclei.

One can also construct a variety of antibonding and of partially bonding molecular orbitals, which should be useful mostly in describing excited or repulsive states of molecules. (Examples of antibonding orbitals: σ^*2p in N_2, cf. II; C−C antibonding orbitals $[x-x]$ in C_2H_4, —cf. III, also section 8*b* (below).)

In case degenerate (atomic or) molecular orbitals, not all in closed shells, are present in the U's of Eq. (1), one must take care to form the ψ's as linear combinations of the U's in such a way that each is a representation of the symmetry group of the molecule. The method is similar to that used for atoms[8] or diatomic molecules when degenerate orbitals are present. [Usually in the present method atomic orbitals, corresponding to unshared electrons, occur only in closed shells and so cause no trouble even if degenerate.] If only nondegenerate molecular orbitals are present, and all atomic orbitals are in closed shells, linear combinations of U's need to be taken only to remove spin degeneracy,[8] and each resultant ψ is then always a representation of the symmetry group *if the molecular orbitals are.* If all orbitals occur only in closed groups (cf. II, page 51), whether atomic or molecular, one has always the identical representation. The truth of these statements can be proved by reasoning similar to that applied to a similar matter in section 2*a*, but rather simpler. The examples to be found in section 8*d* (cf. Eqs. (9–12) should also be instructive.

2c. Construction of molecular orbitals as linear combinations of atomic orbitals. The manner in which molecular orbitals can be constructed from atomic orbitals so as to conform to definite representations of the molecular group can be seen from some examples (cf. also I, II, III, etc.). Thus, molecular orbitals of H_2^+ can be formed as sums (bonding, types σ_g, π_u, etc.) or differences (antibonding, types σ_u, π_g, etc.) of H atom orbitals, namely *const.* $(\varphi_A+\varphi_B)$ or *const.* $(\varphi_A-\varphi_B)$, where φ_A and φ_B refer to equivalent orbitals of the two H nuclei.

As a simple example of a polyatomic case, a certain bonding orbital of CH_2 (or H_2O), belonging to the identical representation a_1 of point group $\mathbf{C_{2v}}$ (cf. Tables I, Ia), and related to the carbon (or oxygen) atomic orbital $2p_z$, can be approximated as follows (cf. Eq. (8) in section 8*a* for other CH_2 or H_2O orbitals):

$$[z]=a(2p_z)+b(\alpha+\beta)+c(2s)+\cdots. \qquad (3)$$

Here α and β refer to 1*s* orbitals of two H atoms placed at equal distances from the C or O atom, while 2*s* and $2p_z$ refer to orbitals of the latter. Equality of the coefficients of α and β is necessary

here in order to have the molecular orbital $[z]$ conform to a_1 of $\mathbf{C_{2v}}$, while the relative signs of a and b must be such that, in the regions where α and β strongly overlap $2p_z$, they have the same sign as the latter. In Eq. (3), c is relatively small in the case of H_2O, but larger in that of CH_2. The ratios b/a and c/a are undetermined coefficients. An antibonding orbital would be obtained if the coefficient b were taken with reversed sign; at the same time the relative magnitudes of a, b, c would be more or less changed.—It may be remarked that the symmetry type $\mathbf{C_{2v}}$ is so simple that everything can be easily seen and worked out without using group theory. For molecules of higher symmetry, however, the group theory treatment is very convenient.

In regard to the possibility of improving the approximation given by Eq. (3), by adding further terms such as $d(3s)$, $e(3p_z)$, $f(3d_z)$, the reader is referred to an illuminating discussion by Slater which is applicable here (reference 9, page 1111). In general, it is profitable only to include atomic orbitals which are fairly much alike in energy. (In the case of H_2O, even the term $c(2s)$ in Eq. (3) could probably better be dropped.) Exact equality of energy of all the orbitals, such as one has in H_2^+, is not necessary.

In Eq. (3) each of the terms $a(2p_z)$, $c(2s)$, and $b(\alpha+\beta)$, separately conforms like $[z]$ itself to representation a_1 of $\mathbf{C_{2v}}$. Such a relation is usual in cases like Eq. (3) where a molecular orbital is built up around an orbital (here $2p_z$) of a central or dominant atom. Further examples (NH_3 and CH_4 types) will be found in V. Only such orbitals of the dominant atom as conform to the final desired representation can be used, for example $2p_z$ and $2s$, but not $2p_x$ or $2p_y$, in Eq. (3).

Often the inclusion of more than one orbital of the dominant or central atom yields a hybrid orbital which gives increased overlapping with the orbitals of the other atoms and so gives stronger bonding. This fact can often be used as a guide in forming a qualitative estimate of the relative magnitudes of two coefficients such as c and a in Eq. (3). One could indeed systematically seek out the "best bonding" hybrid orbitals of the central atom, i.e., orbitals giving maximum overlapping with those of the outer atoms to be bound, as Pauling has done[12] in connection with electron-pair bonds.[13]

One has, however, in general no right to assign to two coefficients like a and c in Eq. (3) such relative values as would correspond to a BBH (best bonding hybrid). In general, if $a_B\varphi_1+c_B\varphi_2$ represents a BBH, then to get a best approximation in Eq. (3), it is correct to use the ratio c_B/a_B only if φ_1 and φ_2 are actually degenerate. If φ_1 and φ_2 are only approximately degenerate, the ratio must be less (or greater), and must approach zero (or infinity) as φ_1 and φ_2 become more unequal in energy. Clearly, however, the larger energy decrease obtainable from stronger bonding weights the scales in favor of hybrids which approximate BBH's.

In seeking approximations corresponding to valence theory, Pauling's procedure for electron-pair bonds is to use alternatively either a BBH or a simple atomic orbital according as it appears probable from chemical and other evidence that the former or the latter gives the better approximation; he does not use intermediate types. This procedure is indeed unavoidable if a *simple* approximation is to be obtained in terms of electron-pair bonds, but it is evidently at a disadvantage in this respect as compared with the present more flexible and (when desirable) more noncommittal method; and it is more subject to possible errors of judgment. The present method has even a certain advantage in having less that it must predict or decide, for this makes it better able to be guided by empirical, including spectroscopic, data. The problem of the structure of the double bond (cf. III, and section 8 below), and of the structure of NH_3, to be discussed in V, are examples of this.

Application of Group Theory

3. Objects and notation

First we might seek to determine the irreducible representations (cf. section 1) for each kind of symmetry that is possible for a polyatomic molecule. Most, at least, of the symmetry types likely to be found in actual molecules, as well,

[13] When a hybrid $a\psi_1+c\psi_2$ of two orbitals is formed, there is of course also another one orthogonal to it, $c\psi_1-a\psi_2$. Of these two hybrid orbitals, one may be well adapted to binding in one direction, the other in another.

apparently, as a number not likely so to occur, are included among those of the 32 crystal classes. Symmetry types with n-fold axes, with $n=5$, 7, 8, or more, are not included. Table I in section 4 gives the representations for all the symmetry types of the 32 crystal classes. If the representations for other types should be needed (e.g., the ring molecule C_5H_{10} may have a five-fold axis), they can be obtained by the same methods (cf. section 4) used for the 32 crystal classes.

For each crystal class there is a symmetry group, composed of all the operations to which the crystal or molecule could be subjected without changing its appearance or aspect viewed from any fixed position.[14] Such symmetry groups are often called point groups.[14] The 32 point groups, it may be noted, correspond to a considerably smaller number of abstract groups, since many of the point groups are, when considered abstractly, identical with others.

The results, as already obtained by Bethe and Wigner (cf. section 1) but arranged somewhat differently to suit the present application, are given in Table I. The different representations of each group are designated by symbols usually the same as those used by Placzek for molecular vibrational states. As noted in section 1, this has advantages over Bethe's simple listing of representations as $\Gamma_1, \Gamma_2, \cdots, \gamma_1, \gamma_2, \cdots$.

Although for the symmetry group of an atom or of a diatomic or linear molecule the number of representations is infinite (s or S, P or p, $D, \cdots$; Σ^+ or σ, Σ^-, Π or $(\pi, \Delta, \cdots)$, it is finite and rather small for all the 32 point groups. For designating the representations of these, capital letters are used here for resultant electronic states (ψ's), small letters for orbitals (φ's), just as for atoms and diatomic molecules. The multiplicity of resultant states is denoted by a left-hand superscript as for atoms and diatomic molecules. No attempt will be made for the present to develop a notation for multiplet components or spin fine structure; it should be noticed that the numerical subscripts $_1$, $_2$, and $_3$ used here for certain representations belong to the *orbital* description. [Cf. Bethe[6] for a treatment of the spin structures.]

In Table I the same symbols are often used for different point groups, but each symbol has, at least in part, a rather definite significance. Thus A, B, a, b refer to nondegenerate, E, e to twofoldly degenerate, T, t to threefoldly degenerate, states or orbitals. A or a means symmetrical, B or b antisymmetrical, for a rotation of $2\pi/n$ around the (or an) n-fold principal axis. (If there is no axis, A is used.) The subscripts $_1$ and $_2$ have varying meanings; superscripts $'$ and $''$ mean symmetrical and antisymmetrical for reflection in a plane (σ_h) perpendicular to the principal axis.

Besides using general symbols such as A_1, a_2, $b_2 \cdots$ analogous to S, p, π, etc., we shall of course feel free to add more specific symbols to describe particular states or orbitals, just as we use symbols like $3p$, $2p\pi$, etc., for atoms and diatomic molecules. In particular we shall use, as already in I, II and III, a variety of symbols such as $[s]$, $[2p_x]$, $[\sigma]$, $[\pi]$, $3d_\beta$, and so on, which indicate that the molecular orbital in question is derived from, or related to, some particular type of atomic or diatomic orbital.

The objects of the following sections, insofar as group theory problems are concerned, may be summarized as follows: (1) to give all the types of electronic states (corresponding to the irreducible representations) for the 32 point groups; (2) to determine the selection rules for these; (3) to determine the nature of the resultant electronic states corresponding to any given electron configuration (e.g., $a_1^2a_2b_1e^3$); (4) to determine what happens to the orbitals and states of a molecule of given symmetry when the symmetry is altered; (5) to find what relations exist between the electronic states of a molecule and those of its (atomic or molecular) dissociation products, for various modes of dissociation. The results for (1), (2), (3), and (4) are given below; those for (5) will be considered later. For atoms and diatomic molecules the corresponding results are already well known.

4. Representations of the 32 point groups

Table I can be completely derived with the help of a limited knowledge of the theory of finite groups, not difficult to acquire in connection with a study of some of the examples

[14] For details, cf. e.g., P. P. Ewald, *Handbuch der Physik*, Vol. 24. J. Springer, Berlin, 1927; or R. W. G. Wyckoff, *The Structure of Crystals:* The Chemical Catalog Company, New York, 1931.

given in the table. The meaning of Table I will now be explained briefly, so that it can be used without further knowledge of group theory, also the method of its derivation will be given. Table Ia shows how the symmetries of a number of molecules are distributed among various point groups.

Given a point group whose irreducible representations are desired, one first divides the symmetry elements (i.e., operations), whose total number may be called g, into a number, let us call it r, of group-theory *symmetry classes*[15] (not to be confused with crystal classes) each containing, let us say, h equivalent elements, where h varies from one class to another.[16] Every group includes the element E (identity), which always forms a class by itself, with $h=1$. An important theorem is: *the number of irreducible representations of any group equals* r. One can construct a square table of representations ($\Gamma_1, \Gamma_2, \cdots \Gamma_r$), classes ($E \equiv C_1, C_2, \cdots C_r$), and *characters* ($\chi$) as shown (also cf. Table I for specific examples).

	E	C_2	..	C_r
Γ_1	$\chi_1^{(1)}$	$\chi_2^{(1)}$	..	$\chi_r^{(1)}$
Γ_2	$\chi_1^{(2)}$	$\chi_2^{(2)}$	..	$\chi_r^{(2)}$
..	..	..	..	..
Γ_r	$\chi_1^{(r)}$	$\chi_2^{(r)}$	..	$\chi_r^{(r)}$

Any character $\chi_m^{(j)}$ describes the effect on the representation Γ_j of *any* operation of the symmetry class C_m (the notation $\Gamma_1, \cdots C_2, \cdots$ will be replaced by more specific designations in Table I). In our case the representations define the possible types of electronic wave functions ψ or φ. The representations of the 32 point groups are all either 1-, 2-, or 3-dimensional, which for φ's and ψ's means nondegenerate, twofoldly or threefoldly degenerate.

For a nondegenerate φ or ψ, belonging say to Γ_j, $\chi_m^{(j)}$ is merely a factor by which φ or ψ is multiplied when subjected to a symmetry operation of the class C_m. For a twofoldly degenerate φ or ψ, one has of course a set of two mutually orthogonal wave functions, say φ_1, φ_2. When these are subjected to any symmetry operation of the molecule's point group, each is in general transformed in such a way that one gets a new mutually orthogonal set φ_1', φ_2', where $\varphi_1' = a_{11}\varphi_1 + a_{12}\varphi_2$ and $\varphi_2' = a_{21}\varphi_1 + a_{22}\varphi_2$. The character χ_m for such a φ(or ψ) is merely the sum $a_{11}+a_{22}$ (i.e., the spur of the matrix of coefficients a_{ij}), taken for any operation of the class C_m. The extension to threefoldly degenerate φ's and ψ's is obvious. Important is the fact that $\chi = a_{11} + a_{22}(+a_{33})$ is independent of how one selects the original two (or three) mutually orthogonal φ's or ψ's.

For the class E, $a_{ij}=0$ except that $a_{11}=a_{22}$ $(=a_{33})=1$, always, so that the character $\chi_1^{(j)}$ for any representation Γ_j is always equal to the number of dimensions of the latter. The following relation[16] then suffices to determine, for any group, how many of its r representations there are of each number of dimensions:

$$(\chi_1^{(1)})^2 + (\chi_1^{(2)})^2 + \cdots + (\chi_1^{(r)})^2 = g. \qquad (4)$$

Every symmetry group has a one-dimensional representation, called the *identical representation*,[15] always symbolized by A, A_1, or A_{1g} in Table I, for which every χ is $+1$, so that any φ or ψ belonging to it has the same symmetry as the nuclear skeleton itself, as is not true of any other representation.

For most of the point groups the χ's are all integers (cf. Table I), but for a few, some of them are complex numbers. In general, φ's or ψ's belonging to different representations cannot have equal energy except in isolated special cases, and n-foldly degenerate φ's or ψ's ordinarily appear only for n-dimensional representations. But when the χ's are complex, one finds that some of the representations occur in pairs, such that the χ's of one member of a pair are conjugate complex to those of the other (cf. e.g., the groups $\mathbf{C_3}$, $\mathbf{C_4}$ in Table I). One can then readily show that the two representations of such a pair are conjugate complex to each other (φ or $\psi = A \pm Bi$); and from this it follows[4] by insertion in the Schrödinger equation (if possible magnetic interactions are neglected) that A and B, and so $A \pm Bi$, etc., are equal in energy and so should be considered as belonging to a single degenerate state.

[15] For a convenient survey of the application of group theory to atomic and diatomic problems, cf. B. L. van der Waerden, *Die gruppentheoretische Methode in der Quantenmechanik*, J. Springer, Berlin, 1932. Also Wigner's book and Eckart's article in Rev. Mod. Phys. for atomic problems.

[16] Cf. pages 11, 76, 77 of reference 15. Placzek[5] uses a similar method without group theory.

TABLE I. *Irreducible representations of the 32 point groups.*

Triclinic

$\mathbf{C_1}$	E
A	1

Also $\mathbf{C_i} = \mathbf{C_1} \times i$

Monoclinic

$\mathbf{C_2}$; *Co*		E	C_2
	$\mathbf{C_s}$	E	$iC_2 = \sigma$
A; z	A'	1	1
B; x or y	A''	1	−1

Also $\mathbf{C_{2h}} = \mathbf{C_2} \times i$

Orthorhombic

$\mathbf{V} \equiv \mathbf{D_2}$; *Co*		E	$C_2(z)$	$C_2(y)$	$C_2(x)$
	$\mathbf{C_{2v}}$	E	$C_2(z)$	$iC_2(y) = \sigma_v$	$iC_2(x) = \sigma_v$
A_1	A_1	1	1	1	1
B_1; z	A_2	1	1	−1	−1
B_2; y	B_1	1	−1	1	−1
B_3; x	B_2	1	−1	−1	1

Also $\mathbf{V_h} \equiv \mathbf{D_{2h}} = \mathbf{V} \times i$

Tetragonal

$\mathbf{D_4}$; *Co*	E	C_2	$2C_4$	$2C_2$	$2C_2'$
$\mathbf{C_{4v}}$	E	C_2	$2C_4$	$2iC_2 = \sigma_v$	$2iC_2' = \sigma_d$
$\mathbf{V_d} \equiv \mathbf{D_{2d}}$	E	C_2	$2iC_4 = 2S_4$	$2C_2$	$2iC_2' = \sigma_d$
A_1	1	1	1	1	1
A_2; z	1	1	1	−1	−1
B_1	1	1	−1	1	−1
B_2	1	1	−1	−1	1
E; $x \pm iy$	2	−2	0	0	0

$\mathbf{C_4}$; *Co*	E	C_2	C_4	C_4^3
$\mathbf{S_4}$	E	C_2	S_4	S_4^3
A; z	1	1	1	1
B	1	1	−1	−1
E; $x \pm iy$	1	−1	$-i$	i
	1	−1	i	$-i$

Also $\mathbf{D_{4h}} = \mathbf{D_4} \times i$, and $\mathbf{C_{4h}} = \mathbf{C_4} \times i$

Hexagonal

$\mathbf{D_6}$; *Co*			E	C_2	$2C_3$	$2C_6$	$3C_2$	$3C_2'$
	$\mathbf{C_{6v}}$		E	C_2	$2C_3$	$2C_6$	$3iC_2 = 3\sigma_d$	$3iC_2' = 3\sigma_v$
		$\mathbf{D_{3h}}$	E	$iC_2 = \sigma_h$	$2C_3$	$2iC_6 = 2S_6$	$3C_2$	$3iC_2' = 3\sigma_v$
A_1	A_1	A_1'	1	1	1	1	1	1
A_2; z	A_2	A_2'	1	1	1	1	−1	−1
B_1	B_2	A_1''	1	−1	1	−1	1	−1
B_2	B_1	A_2''	1	−1	1	−1	−1	1
E^*	E_1^*	E'	2	2	−1	−1	0	0
E_1^*; $x \pm iy$	E_2^*	E''	2	−2	−1	1	0	0

$\mathbf{C_6}$; *Co*	E	C_6	C_3	C_2	C_3^2	C_6^5
A	1	1	1	1	1	1
B	1	−1	1	−1	1	−1
E^*	1	ω^2	$-\omega$	1	ω^2	$-\omega$
	1	$-\omega$	ω^2	1	$-\omega$	ω^2
E_1^*	1	ω	ω^2	−1	$-\omega$	$-\omega^2$
	1	$-\omega^2$	$-\omega$	−1	ω^2	ω

Note: $\omega = e^{2\pi i/6} = -\omega^4$

Also $\mathbf{C_{6h}} = \mathbf{C_6} \times i$; also $\mathbf{C_{3h}} = \mathbf{C_3} \times \sigma_h$, with states A', A'', E', E''

TABLE I. (*Continued*).

Rhombohedral

D3; *Co*	*E*	$2C_3$	$3C_2'$
C3v	*E*	$2C_3$	$3iC_2'=3\sigma_v$
A_1	1	1	1
A_2; *z*	1	1	−1
E; $x\pm iy$	2	−1	0

C3	*E*	C_3	C_3^2
A	1	1	1
E	1	ω	ω^2
	1	ω^2	ω

Note: $\omega=e^{2\pi i/3}$

Also **D3d** = **D3**×*i*; **C3i** ≡ **S6** = **C3**×*i*

Cubic

O; *Co*	*E*	$3C_2$ (*x*, *y*, *z*)	$6C_4$	$6C_2$	$8C_3$
Td	*E*	$3C_2$	$6iC_4=S_4$	$6iC_2=6\sigma_d$	$8C_3$
A_1	1	1	1	1	1
A_2	1	1	−1	−1	1
E	2	2	0	0	−1
T_1; (*x*, *y*, *z*)	3	−1	1	−1	0
T_2	3	−1	−1	1	0

T	*E*	$3C_2$	$4C_3$	$4C_3'$
A	1	1	1	1
E	1	1	ω	ω^2
	1	1	ω^2	ω
T	3	−1	0	0

Note: $\omega=e^{2\pi i/3}$

Also **Oh** = **O**×*i*; **Th** = **T**×*i*

Besides Eq. (4), two further relations[17] can be given by means of which the characters for all the possible representations of any finite group can be completely determined. The results given in Table I have been obtained[4, 6] in this way. For the various characters of any one representation (cf. the small table above on page 287)

$$\sum_{i=1}^{r} h_i\chi_i\bar{\chi}_i=g, \tag{5}$$

where $\bar{\chi}_i$ is the complex conjugate of χ_i; and also

$$h_ih_k\chi_i\chi_k=\chi_1\sum_{l=1}^{r}c_{(ik)l}h_l\chi_l, \tag{6}$$

where the coefficients $c_{(ik)l}$ are those which appear when one takes the "product of two classes" C_i and C_k (cf. reference 15, p. 170):

$$C_iC_k=C_kC_i=\sum_{l=1}^{r}c_{(ik)l}C_l. \tag{6a}$$

In order to use Eq. (6*a*) it is of course necessary to have a multiplication table of products of classes C_iC_k (including the case $i=k$). Such tables can be constructed by obvious methods when needed, for any symmetry group (cf. reference 6).

Explanation of tables. At the top of each table are given at the left (**bold-faced type**) the point groups to which it applies, at the right (*italic type* the elements of symmetry belonging to each point group. The notations for the point groups and for the symmetry elements are essentially those of Schönflies,[14] except that in the case of certain elements (reflections and rotary-reflections) an additional designation of the form iC_n (cf. Bethe[6]), showing how the element could be obtained as the product of a pure rotation C_n and the inversion *i*, is given for convenience. [In some cases also a ′ or an *x*, *y*, or *z* has been added to help make clear the exact operation which is meant; Ewald[14] gives complete details as to the various operations. In every case the (or a) principal axis of symmetry is called the *z* axis,—even in the monoclinic system, where the axis is usually called *y*.] The symmetry elements are arranged in symmetry classes according to group theory[17] the number preceding the symbol for any symmetry element being the *number h* of equivalent elements of this kind forming the class (if no number is given, $h=1$). The *total number* *g* of symmetry elements belonging to any point group can be obtained by adding the *h*'s, e.g., $g=2$ for **C2** and **Cs**, 8 for **D4**. *In the main* and lower part of each table are given at

[17] Cf. A. Speiser, *Die Theorie der Gruppen von endlicher Ordnung*, second edition (J. Springer, Berlin, 1927), especially Chaps. 1, 2, 11, 12; cf. p. 28 for definition of a class, pp. 174–6 for Eqs. (4)–(6*a*). For an explanation of the relations of group theory to the present problem, reference 6 is valuable (cf. also reference 4).

the left the symbols, and at the right the characters χ, of all the irreducible representations of the point groups designated at the top of the table.

Outside each table are indicated one or two point groups not included in the table, e.g., $\mathbf{D_{6h}}$ in the case of the hexagonal table. Each of these contains the same symmetry classes as for some group in the table, plus an equal number of others each generated by multiplying one of the original set by the operation i (inversion), or in one case by σ_h. For example $\mathbf{D_{6h}} = \mathbf{D_6} \times i$ has all the six classes E, C_2, $2C_3$, etc. of $\mathbf{D_6}$ plus the six classes i, iC_2, $2iC_3$, etc. Each point group $\mathbf{G} \times i$ has two irreducible representations for each one of $\mathbf{G}$. For example, corresponding to A_1, A_2, etc. of $\mathbf{D_6}$ one has for $\mathbf{D_{6h}}$ the representations A_{1g}, A_{1u}, A_{2g}, A_{2u}, etc. A_{1g} and A_{1u} have the same characters as A_1 for the symmetry classes E, C_2, $\cdots$ common to $\mathbf{D_6}$ and $\mathbf{D_{6h}}$, while the characters of A_{1g} and A_{1u} for the classes i, iC_2, etc. are respectively $+1$ and -1 times the characters of A_1 for the classes E, C_2, etc. Similar relations hold for A_{2g}, A_{2u}, and so on.

For use in connection with the determination of selection rules, the behavior of the coordinates x, y, z under the *rotational operations* of each crystal system (monoclinic, triclinic, etc.) is given in the table or tables for that system (*heading Co*, and *symmetry classes as given in first line of table*). The behavior of each coordinate, or of a pair $(x \pm iy)$ or set of three (x, y, z in the cubic system only) of coordinates which are equivalent, is given by a set of characters whose correctness the reader can easily verify. Every such set of characters is found to agree with that of some representation in the table (cf. tables). For the operation i *the character for a coordinate or set of these* is always just the negative of that for operation E, and *for any symmetry class* niC_m it *is always just the negative of that for* nC_m.

TABLE Ia. *Some probable examples of molecules having symmetries belonging to various point groups.*

$\mathbf{C_s}$: NOCl, C_2H_4 derivatives like C_2H_3Cl, C_2H_2ClBr, $C_2HClBrI$. $\mathbf{C_2}$: perp. $C_2H_2Cl_2$. $\mathbf{C_{2h}}$: plane *trans*-$C_2H_2Cl_2$. $\mathbf{C_{2v}}$: plane *cis*-$C_2H_2Cl_2$, $(Cl_2C)CH_2$, CH_2Cl_2, H_2O_2, H_2O, NO_2, SO_2, NH_2Cl, HCHO. $\mathbf{V}$: partly rotated C_2H_4. $\mathbf{V_h}$: plane C_2H_4. $\mathbf{V_d}$: perp. C_2H_4. $\mathbf{D_{4h}}$: $PtCl_4^{=}$. $\mathbf{C_{4v}}$: distorted $PtCl_4^{=}$ (Pt out of plane). $\mathbf{D_{6h}}$: C_6H_6. $\mathbf{C_{6v}}$: C_6H_6 with planes of C and H displaced. $\mathbf{D_{3h}}$: NO_3^-, O_3 (if triangular), C_2H_6 when trigonal. $\mathbf{D_3}$, $\mathbf{D_{3d}}$: rotated forms of C_2H_6. $\mathbf{C_{3v}}$: NH_3, ClO_3^-, CH_3F, PCl_3(?) $\mathbf{T_d}$: CH_4, MnO_4^-. $\mathbf{O_h}$: SF_6, $PtCl_6^{=}$.

5. Selection rules

One can easily obtain the polarization and selection rules which limit transitions between the electronic states of a molecule conforming to any point group in Table I. To do this, one makes use of the fact that the coordinates x, y, z themselves,—or combinations of equivalent coordinates, e.g., (x, y) or $(x \pm iy)$, which are analogous to degenerate φ's or ψ's,—always belong like the φ's and ψ's to definite representations of the point groups, and can be characterized by sets of χ's (cf. Table I, and last paragraph of "Explanation" following it). To find out with what states a given state with wave function ψ_i can combine, for an electric moment Q, one makes use of the expansion[16]

$$Q\psi_i = \Sigma a_{ij}\psi_j. \tag{7}$$

Here Q is proportional in the case of one electron, for dipole transitions, to x, y, or z, or to a combination $(x+iy, x-iy)$ or (x, y, z); or if there are several electrons one replaces for example x by a sum of x's, and so on. Every transition $\psi_i \leftrightarrow \psi_j$ is allowed for which a Q can be found giving $a_{ij} \neq 0$ in Eq. (7), but it is forbidden if $a_{ij} = 0$ for all Q's. If $a_{ij} = 0$ for all but one Q, the transition is polarized accordingly. Selection rules for quadrupole and other transitions can be obtained by using suitable expressions for Q. Selection rules obtained as above, of course, apply also to vibrational[5] and electronic $\times$ vibrational transitions.

In order to determine selection rules, Eq. (7) is applied in the following way. For any ψ_i belonging to any irreducible representation of a given point group, and for a given Q, one first determines for the product $Q\psi_i$ a set of characters, by multiplying the character of ψ_i for each symmetry class by the character of Q for the same class.

Very often the resulting set of characters of $Q\psi_i$ is at once identified as belonging to one of the irreducible representations of the group; this happens whenever Q or ψ_i, or both, belong to one-dimensional representations. This means that only ψ_j's which belong to the representation thus identified have $a_{ij} \neq 0$ in Eq. (7), and only

such ψ_j's can combine with ψ_i with a moment of the type Q.

Example: let Q be z and let ψ_i belong to representation B_1 of point group $\mathbf{C_{4v}}$, cf. Table I, tetragonal system. Multiplying the character-systems of z and B_1, the resulting character-system is seen to be that of B_1, since in this case z belongs to the identical representation (characters 1, 1, 1, 1, 1).[To get the correct result, one must take care to notice that the signs of the characters of z, for the operations iC_2 and iC_2', must be reversed as compared with those given in the table, since the latter apply to the operations C_2 and C_2' (cf. last paragraph of explanation under Table I). A similar precaution must be taken in other cases too.] Hence one concludes that for a z moment, states (φ's or ψ's) belonging to B_1 can combine only with other states belonging to the same representation. Similarly one finds that for electric moments $x+iy$, states of type B_1 can combine only with those of type E. One sees thus that for dipole transitions the B_1 type combines only with types B_1 and E. The reader can easily determine the selection rules for A_1, A_2, and B_2 states by the same method.

Whenever Q and ψ_i both belong to representations which are more-than-one-dimensional, the system of characters obtained for Q_i is not that of an irreducible representation. In this case one has to resolve each character of $Q\psi_i$ into a sum of characters, in such a way that the resulting (two or more) sets of characters are those of irreducible representations. Such a resolution is always possible, and the result is unique.

Example: let Q be $x\pm iy$ and let ψ_i belong to E of $\mathbf{C_{4v}}$. The character-system (4, 4, 0, 0, 0) of the product $(x\pm iy)\psi_E$ is seen to be the sum of those of the representations A_1, A_2, B_1, and B_2 of $\mathbf{C_{4v}}$. We conclude that states belonging to E can combine, for a moment $x\pm iy$, with all these four types. From the characters of $z\psi_E$ one concludes further that for a z moment, states of type E can combine only with other states of type E.

For any point group $\mathbf{G}\times i$, the types of states are the same as for group $\mathbf{G}$, except that there is one $_g$ and one $_u$ representation for each representation of group $\mathbf{G}$ (cf. "Explanation of tables" under Table I for details). It is easily shown by making use of the fact that every Q of type x, y, z or $x\pm iy$ changes sign under the operation i, that for dipole transitions one has for any group $\mathbf{G}\times i$ just the same selection rules as for the corresponding group $\mathbf{G}$, *plus the rule* $g\leftrightarrow u$ ($g\leftrightarrow g$, $u\leftrightarrow u$ forbidden). This is the same rule which holds for all systems having a center of inversion (atoms, electronic ψ of homopolar diatomic molecules, total ψ of any molecule, etc.).

5a. Franck-Condon principle. The electronic selection-polarization rules derived in section 5 hold strictly only for the case that the symmetry of the molecule belongs to the same point group in the initial and final states. (Changes of dimensions not causing a change in the point group do not, however, affect the selection rules.) The most probable transitions, according to the Franck principle, are those in which the nuclear configuration does not change its dimensions or velocities. Since even moderately large deviations from the Franck principle, which occur only with low probability, would rarely if ever cause more than a moderate break-down in the electronic selection rules, we conclude that, for any given initial state, in emission or absorption, transitions which violate the electronic selection rules belonging to the point group of this initial state should occur only with very low, usually negligible, intensity.

In the case of electronic transitions which do *not* violate the selection rules of the initial point group, the extent of deviations from the predictions of the Franck-Condon rule strictly applied, should presumably be similar to that in diatomic molecules. For an initial state without nuclear vibration or internal rotation, the application of the Franck-Condon principle shows that in many cases an electronic change may result in high-amplitude vibrations or internal rotations (cf. III for an example). These may give rise to large changes in the arrangement of the nuclei, but this makes little difference for the electronic selection rules, since according to Franck these depend mainly on what happens at the instant the light quantum is absorbed or emitted, before the nuclei have had time to move much.

If one has an initial state of high-amplitude vibration or internal rotation such that the nuclei are continually passing through a variety of configurations, one must determine what the

selection rules are for each different point group whose symmetry the nuclei take on. Only such electronic selection rules as are common to all the different configurations are strict. Furthermore, if as usual there are preferred configurations in which the nuclei spend most of their time, and if these, but not intermediate, configurations, demand certain selection rules, then these rules must hold approximately.—In dealing with all such cases, one needs of course to know the rules for correlating electronic states of different point groups (cf. section 6, paragraph just before Table II, but also section 8*c*).

6. Resolution of representations of symmetry groups (atomic and molecular) into those of groups of lower symmetry

An important problem is the resolution of a reducible representation into irreducible ones.[15, 17] An example where this problem occurs, and the very simple method of solving it, have been given in section 5. Other important examples occur when, starting with a physical system having relatively high symmetry, the symmetry is altered in such a way that the new symmetry group is a subgroup of the old one, i.e., is a group containing just a part of the symmetry elements of the old group, but no new ones. Examples are: (*a*) an atom subjected to a perturbing electric field, as in a crystal[6] or as in the formation of a molecule; or imagined modified by the splitting of its nucleus to give a diatomic or polyatomic molecule; (*b*) a molecule of high symmetry distorted to one of lower symmetry, for example tetrahedral CH_4 deformed by pulling one H atom out of position.

In many cases, degenerate representations split up partly or wholly when the symmetry of a molecular system is decreased, but the total number of different irreducible representations generally decreases. The new representations can be obtained by the following method. One tests the effect of each class of symmetry elements of the *new group* on any desired representation (or specifically on a particular φ or ψ) of the old group, and writes down the resulting set of characters. If the original representation was nondegenerate, this set of characters is at once identified as belonging to a definite representation of the new group. Otherwise, one has a reducible representation which can be resolved into a sum of irreducible representations of the new group by the method stated in section 5 (second from last paragraph). The result is always unique.[15, 17] Examples are given by Bethe,[6] and in the following Tables II–IV.

In the course of the present work, it will be convenient for various purposes to have reduction tables showing how atomic→polyatomic, diatomic→polyatomic, and polyatomic→polyatomic representations of lower symmetry. Tables II–IV are not complete, but cover a number of the cases most likely to be needed. Other results can be worked out easily when needed (cf. Table II, note *c* and Table III, notes *a*, *d*, *e*). The tables with their notes are self-explanatory.

In using any table, care should be taken to be sure that the relations between the axes of the two groups with which one is concerned are the same as in the table. Otherwise the table is not applicable. In the tables, the only cases given are those where the z axes of the more and the less symmetrical group with which any table deals are coincident. Such cases are the most common in practice.

Sometimes one has two symmetry groups with some elements in common, others peculiar to each, and wishes to know in what way the representations of the one group would go over into those of the other if the symmetry were altered from the one to the other case. An *example* is the correlation of energy levels between the states of plane and "perpendicular" C_2H_4 (cf. III, and section 8*c* below). In such cases, just those symmetry elements which are common to the two groups are also possessed by the symmetry group corresponding to an arrangement of nuclei intermediate between those of the two original cases. One then reduces the representations of each of the latter in terms of those of the intermediate group, which is a sort of greatest common factor. Then one applies the usual rule for adiabatic correlations, namely that these are so made that, on the energy-level diagram, no two lines cross which denote states belonging to the same representation of the intermediate symmetry group.

Explanation of Table IV. The meaning of the tables should be clear from the following detailed

interpretation of the fifth small table, headed $\mathbf{D_{4h}}\,|\,\mathbf{V_h}\ \mathbf{V_d}\ \mathbf{C_{4v}}$. This table shows what each of the ten representations of $\mathbf{D_{4h}}$ goes over into if the symmetry is reduced to $\mathbf{V_h}$, or $\mathbf{V_d}$, or $\mathbf{C_{4v}}$. For example, A_{1g}, A_{1u}, A_{2g}, etc., of $\mathbf{D_{4h}}$ go over respectively into A_{1g}, A_{1u}, B_{1g}, etc. of $\mathbf{V_h}$, or into A_1, B_1, A_2, etc. of $\mathbf{V_d}$, or into A_1, A_2, A_2, etc. of $\mathbf{C_{4v}}$. Also obviously (not in the tables) A_{1g} and A_{1u} of $\mathbf{D_{4h}}$ would go into A_1 of $\mathbf{D_4}$, and so on. Table IV is by no means complete; other reductions when needed can easily be obtained, as were those given, by methods described in sections 6, 5. In all cases the z axes of the two groups considered are taken as coincident; otherwise different results would in general be obtained. In some cases ($\mathbf{C_{4v}}\rightarrow\mathbf{C_{2v}}$, $\mathbf{C_{6v}}\rightarrow\mathbf{C_{3v}}$) the result depends also on which of two sets of vertical planes of the larger group is identified

TABLE II. *Resolution of atomic representations into irreducible representations of molecular symmetry groups.*

Atom	$\mathbf{O_h}$	$\mathbf{T_d}$	$\mathbf{D_{6h}}$	$\mathbf{C_{3v}}$	$\mathbf{D_{4h}}$	$\mathbf{C_{2v}}$
	(all g, u)		(all g, u)		(all g, u)	
$\mathbf{S_g}$, $\mathbf{S_u}$	A_1	A_1, A_2	A_1	A_1, A_2	A_1	A_1, A_2
$\mathbf{P_g}$, $\mathbf{P_u}$	T_1	T_1, T_2	$A_2+E_*^*$	A_2+E, A_1+E	A_2+E	$A_2+B_1+B_2$, $A_1+B_1+B_2$
$\mathbf{D_g}$, $\mathbf{D_u}$	$E+T_2$	$E+T_2$, $E+T_1$	A_1+E^* $+E_*^*$	A_1+2E, A_2+2E	A_1+B_1 $+B_2+E$	$2A_1+A_2+B_1+B_2$, $A_1+2A_2+B_1+B_2$

Notes: (*a*) S_g, S_u, P_g, P_u, D_g, D_u are usually written S, S^0, P, P^0, D, D^0. (*b*) The table holds also for orbitals as follows: s behaves like S_g, p like P_u, d like D_g. (*c*) The results for $\mathbf{O_h}$, $\mathbf{D_{6h}}$, and $\mathbf{D_{4h}}$ are from reference 6, while the remaining results, and any desired results for other point groups, can be obtained from those for $\mathbf{O_h}$, $\mathbf{D_{6h}}$, and $\mathbf{D_{4h}}$ by using Tables I and IV. (*d*) Bethe[6] gives additional results, for the relations between F, G, . . . atomic states and the representations of $\mathbf{O_h}$, $\mathbf{D_{6h}}$, and $\mathbf{D_{4h}}$. (*e*) For the relations between atomic and diatomic (or linear-molecule) representations, cf. Wigner and Witmer, Zeits. f. Physik **51**, 859 (1928); or reference 15 or Mulliken, Rev. Mod. Phys. **4**, 1932 (bottom page 20).

TABLE III. *Resolution of representations of diatomic (or linear-molecule) groups* $\mathbf{C_{\infty v}}$ *and* $\mathbf{D_{\infty h}}$ *into those of some other molecular symmetry groups.*

$\mathbf{D_{\infty h}}$	$\mathbf{D_{6h}}$	$\mathbf{C_{6v}}$	$\mathbf{C_{3v}}$	$\mathbf{D_{4h}}$	$\mathbf{C_{4v}}$	$\mathbf{C_{2v}}$
$\Sigma^+_{g,\,u}$	A_{1g}, A_{2u}	A_1	A_1	A_{1g}, A_{2u}	A_1	A_1
$\Sigma^-_{g,\,u}$	A_{2g}, A_{1u}	A_2	A_2	A_{2g}, A_{1u}	A_2	A_2
$\Pi_{g,\,u}$	$E^*_{2g,\,u}$	E^*_2	E	$E_{g,\,u}$	E	B_1+B_2
$\Delta_{g,\,u}$	$E^*_{g,\,u}$	E^*	E	$B_{1g,\,u}+B_{2g,\,u}$	B_1+B_2	A_1+A_2
$\Phi_{g,\,u}$	$B_{1g,\,u}+B_{2g,\,u}$	B_2+B_1	A_1+A_2	$E_{g,\,u}$	E	B_1+B_2
$\Gamma_{g,\,u}$	$E^*_{g,\,u}$	E^*	E	$A_{1g,\,u}+A_{2g,\,u}$	A_1+A_2	A_1+A_2

Notes: (*a*) Table III holds only if the symmetry (z) axis of the diatomic case coincides with the z axis of the other case. Other results are obtained for other relations between the axes of the two cases. (*b*) Table III of course applies equally well for the corresponding small letters, e.g., $\sigma_{g,\,u}$ behave like $\Sigma^+_{g,\,u}$ and give a_{1g}, a_{2u}, and so on. (*c*) Table III is applicable also (dropping g's and u's) for the resolution of the representations Σ^+, Σ^-, Π, Δ, . . . of the group $\mathbf{C_{\infty v}}$ ($\mathbf{D_{\infty h}}=\mathbf{C_{\infty v}}\times i$) into representations of $\mathbf{C_{6v}}$, $\mathbf{C_{4v}}$, $\mathbf{C_{3v}}$, $\mathbf{C_{2v}}$, etc., but the representations of $\mathbf{C_{\infty v}}$ cannot, of course, be resolved into those of $\mathbf{D_{6h}}$, $\mathbf{D_{4h}}$ or other groups of type $\mathbf{G}\times i$. (*d*) Resolution, when possible, into representations of other point groups can be effected by using first Table III, then Table I. Resolution of representations of $\mathbf{C_{\infty v}}$ and $\mathbf{D_{\infty h}}$ into those of point groups belonging to the cubic system is not possible. Even and odd (g and u) representations of $\mathbf{D_{\infty h}}$ must in general be treated separately. (*e*) In constructing Table III, one needs first an auxiliary table of characters showing how the representations of $\mathbf{C_{\infty v}}$ and $\mathbf{D_{\infty h}}$ behave under various symmetry operations of the point groups. Such a table can easily be constructed by the reader by using the following relations. For the operation E, $\chi=1$ for Σ, 2 for all other states. For a rotation through any angle φ around the z axis, $\chi=1$ for all Σ states, $\chi=e^{i\Lambda\varphi}+e^{-i\Lambda\varphi}=2\cos\Lambda\varphi$ for states with $\Lambda>0$ (Π, Δ, . . . states). For reflection in any plane through the z axis, $\chi=+1$ for Σ^+, -1 for Σ^-, 0 for all other states; σ behaves like Σ^+. (Cf. Wigner and Witmer, Zeits. f. Physik **51**, 862, 1928, or reference 15, p. 40.) These results apply as well to $\mathbf{C_{\infty v}}$ as to $\mathbf{D_{\infty h}}$. For $\mathbf{D_{\infty h}}$ one needs also the following: for operation i, χ is ±1 times its value for E, according as the diatomic state is g or u; for reflection in the xy plane, which is equivalent to i times a rotation of π around the z axis, χ is equal to ±1 (depending on the sign of χ for i) times the χ for the rotation; for rotation by π around any axis perpendicular to the z axis, which is equivalent to i times reflection in any plane passing through the z axis, χ is equal to ±1 (depending on the sign of χ for i) times χ for the reflection, and so, as one easily finds, has the value $+1$ for Σ^+_g and Σ^-_u, -1 for Σ^-_g and Σ^+_u, 0 for all other states.

TABLE IV. *Resolution of polyatomic representations into those of groups of lower symmetry.*

C_{2h}	C_i	C_s
A_g, A_u	A_g, A_u	A', A''
B_g, B_u	A_g, A_u	A'', A'

V_h	C_{2h}	C_{2v}
A_{1g}, A_u	A_g, A_u	A_1, A_2
B_{1g}, A_u	A_g, A_u	A_2, A_1
B_{2g}, A_u	B_g, A_u	B_1, B_2
B_{3g}, A_u	B_g, A_u	B_2, B_1

V	C_2
A_1	A
B_1	A
B_2	B
B_3	B

C_{2v}	C_2
A_1	A
A_2	A
B_1	B
B_2	B

D_{4h}	V_h	V_d	C_{4v}
(all g, u)	(all g, u)		
A_1	A_1	A_1, B_1	A_1, A_2
A_2	B_1	A_2, B_2	A_2, A_1
B_1	A_1	B_1, A_1	B_1, B_2
B_2	B_1	B_2, A_2	B_2, B_1
E	B_2+B_3	E	E

V_d	V	C_{2v}
A_1	A_1	A_1
A_2	B_1	A_2
B_1	A_1	A_2
B_2	B_1	A_1
E	B_2+B_3	B_1+B_2

C_{4v}	C_{2v}
A_1	A_1
A_2	A_2
B_1	A_1 or A_2
B_2	A_2 or A_1
E	B_1+B_2

D_{6h}	D_{3d}	D_{3h}	C_{6v}
(all g, u)	(all g, u)		
A_1	A_1	A_1', A_1''	A_1, A_2
A_2	A_2	A_2', A_2''	A_2, A_1
B_1	A_2	A_1'', A_1'	B_2, B_1
B_2	A_1	A_2'', A_2'	B_1, B_2
E^*	E	E', E''	E^*
E_*^*	E	E'', E'	E_*^*

D_{3h}	C_{3v}
A_1'	A_1
A_2'	A_2
A_1''	A_2
A_2''	A_1
E'	E
E''	E

C_{6v}	C_{3v}
A_1	A_1
A_2	A_2
B_2	A_2 or A_1
B_1	A_1 or A_2
E^*	E
E_*^*	E

D_{3d}	C_{2h}	C_{3v}
(all g, u)	(all g, u)	
A_1	A	A_1, A_2
A_2	B	A_2, A_1
E	$A+B$	E

D_3	C_2
A_1	A
A_2	B
E	$A+B$

C_{3v}	C_s
A_1	A'
A_2	A''
E	$A'+A''$

O_h	D_{4h}	T_d
(all g, u)	(all g, u)	
A_1	A_1	A_1, A_2
A_2	B_1	A_2, A_1
E	A_1+B_1	E
T_1	A_2+E	T_1, T_2
T_2	B_2+E	T_2, T_1

T_d	V_d	C_{3v}
A_1	A_1	A_1
A_2	B_1	A_2
E	A_1+B_1	E
T_1	A_2+E	A_2+E
T_2	B_2+E	A_1+E

with a set of vertical planes of the smaller group; this accounts for the alternatives given in the tables.

7. Determination of possible resultant electron states for various electron configurations

An important problem is that of determining, for a given electron configuration, what are the possible electronic states. For example with a configuration $a_1^2b_2e^3$ of a molecule having the symmetry $\mathbf{C_{4v}}$, these states would be just ^3E and ^1E.

First we may consider the case that the molecule has its electrons all in different, molecular, orbitals. One forms the product, for each symmetry operation, of the characters χ for the various orbitals which are occupied, and thus gets a definite system of characters for the resultant product representation.[6, 15] This either is immediately identified as an irreducible representation of the group, defining the type of the resultant electronic state, or else it can be resolved into a sum of such representations, corresponding to several possible resultant states (cf. sections 5, 6 for the method). The resultant spin has of course all the possible values one would get for the same number of non-equivalent electrons in an atom or diatomic molecule.

Examples: (*a*) given the configuration a_2b_2 of $\mathbf{C_{4v}}$, the product representation is immediately identified as B_1, and the states are $^3B_1$ and $^1B_1$. (*b*) Given $a_2b_1e^*$ of $\mathbf{D_6}$, one gets $^4E_*^*$, $^2E_*^*$, $^2E_*^*$. (*c*) Given $e^*e_*^*$ of $\mathbf{D_6}$, one gets the product character-system 4, -4, 1, -1, 0, 0, and the states $^3B_1$, $^3B_2$, $^3E_*^*$, $^1B_1$, $^1B_2$, $^1E_*^*$.

The same method can be used if one thinks of a molecule as composed of a core plus one or more outer, perhaps valence, electrons. For example,

with point group $\mathbf{C_{4v}}$, a core of type $^3B_2$ plus an outer electron of type e give states ^4E and ^2E.—The same point of view can also often be applied in determining the possible states of a united-system (molecule) in relation to the states of two part-systems (atoms or radicals) which come together. Discussion of such dissociation problems will, however, be postponed.

In a polyatomic molecule a group of $2n$ electrons occupying any n-foldly degenerate molecular orbital functions is a closed shell; it is required by the Pauli principle to have zero resultant spin, and it belongs to the identical representation of the molecule's point group, i.e., all the χ's are $+1$ (cf. fifth following paragraph for proof). The totality of electrons in closed shells composed of molecular orbitals, plus the totality of unshared electrons assigned to closed shells of atomic orbitals (assuming that no atomic closed shell has been removed *in toto* from the molecule), can always be regarded as a core, whose state always belongs to the identical representation with zero spin (cf. fifth following paragraph for proof). From the rule for getting the χ's for a product representation, it is now evident that such a core, since all its χ's are $+1$, can be disregarded in finding the nature of the resultant state of the whole molecule, in the same way that closed shells can be disregarded in the case of atoms or diatomic molecules.—It may also be noted here that, except for their spins, electrons in molecular orbitals belonging to the identical representation (a_1, a_{1g}, etc.) can also be disregarded in determining the resultant state.

Next we must consider the case where, aside from closed shells, two or more equivalent electrons are present in degenerate orbitals. (Two electrons in a nondegenerate orbital of course form a closed shell.) In case both equivalent and non-equivalent electrons are present, one of course first finds the resultant states of each of these separately, then treating the one set of electrons as a core, finds the final resultant states.

Bethe has attacked the problem by a method similar to that customary for the analogous atomic problem. He assumes the molecule, belonging to a specified point group, to be subjected to a perturbing electric field of sufficiently low symmetry so that the degenerate representations of the original group are split up. The Pauli principle can then be applied, and the nature of the allowed states for the desired case determined by resynthesizing the perturbed representations into those of the original group (cf. reference 6, pages 177–180). This method (hereafter called *method A*) is, however, not in general adequate, since the correlations by means of which one goes backward from the perturbed to the unperturbed representations do not always give unambiguous results (cf. e.g., the two alternative sets of Γ's for Bethe's g_5^2 of the tetragonal holohedral and γ_5^2 of the cubic holohedral group), although it is clear that for every set of equivalent electrons there must exist a unique set of resultant electronic states. Unique results can, however, be obtained by using method A in combination with another method (B) described below.

In the monoclinic, triclinic and orthorhombic systems of point groups, all the representations are nondegenerate, so that the present problem does not arise. In the tetragonal, hexagonal, and rhombohedral systems, we must consider cases like e^2, e^3, where e is twofoldly degenerate. In the cubic system we have e^2, e^3, also t^2, t^3, t^4, t^5, where t is threefoldly degenerate. It will be sufficient to consider just the three holohedral point groups $\mathbf{D_{4h}}$, $\mathbf{D_{6h}}$, and $\mathbf{O_h}$, for as can easily be seen, any desired results for other point groups having degenerate representations can be obtained by a process of resolution and comparison, by using Tables IV, I. (An example is given in the third following paragraph.)

Beginning with $\mathbf{D_{4h}}$, *method B* proceeds as in the following example. From Table III we note that π_u, π_g of the diatomic group $\mathbf{D_{\infty h}}$ go over, if the symmetry is reduced to $\mathbf{D_{4h}}$, into e_u, e_g. Likewise π_u^2 and π_g^2 of $\mathbf{D_{\infty h}}$ must go over, for the imaginary case of no coupling between the two electrons, into $(e_u)^2$ and $(e_g)^2$ of $\mathbf{D_{4h}}$. If now one allows some coupling between the electrons, one gets for $\mathbf{D_{\infty h}}$ the states $^3\Sigma^-_g$, $^1\Delta_g$, $^1\Sigma^+_g$ (the same for π_u^2 as for π_g^2). Since these results are independent of the strength of the coupling, these states of $\mathbf{D_{\infty h}}$ must be correlated with the states obtainable from $(e_u)^2$ and $(e_g)^2$ of $\mathbf{D_{4h}}$. Reference to Table III shows that $^3\Sigma^-_g$, $^1\Delta_g$, $^1\Sigma^+_g$ of $\mathbf{D_{\infty h}}$ go over into $^3A_{2g}$, $^1B_{1g}$, $^1B_{2g}$, and $^1A_{1g}$ of $\mathbf{D_{4h}}$, which are, then, the desired possible resultant states

of the configuration $(e_u)^2$, and of $(e_g)^2$. In a similar way, since π_u^3 gives $^2\Pi_u$ and π_g^3 gives $^2\Pi_g$, one concludes that $(e_u)^3$ of $\mathbf{D_{4h}}$ gives ^2E_u and $(e_g)^3$ gives ^2E_g.

In a similar way it follows, from the fact that π_g^4 or π_u^4 gives the identical representation $^1\Sigma^+_g$, that $(e_u)^4$ or $(e_g)^4$ gives $^1A_{1g}$. In an analogous manner, one can easily show, for any point group outside the cubic system, that a molecular closed shell always gives the identical representation of the group. For point groups of the cubic system, a different method, like that used below for such groups, gives a corresponding result.—If one regards as a core the unshared electrons which in the present method are assigned to closed shells of atomic orbitals, it follows from (1) of the proof given in section 2*a* that this core belongs to the identical representation of the molecule's point group, provided equivalent atoms have the same sets of closed shells (as they of course have in saturated molecules). Hence the totality of electrons in such atomic closed shells, together with those in closed shells of molecular orbitals, can be treated as a core which belongs to the identical representation.

If we are interested not in $\mathbf{D_{4h}}$ as above, but for example in $\mathbf{V_d}$, to which perp. C_2H_4 belongs (cf. section 8*b*), one easily finds from Table IV, by resolution of representations of $\mathbf{D_{4h}}$ into those of $\mathbf{V_d}$, that the set of states corresponding to e^2 of $\mathbf{V_d}$ is $^3A_2$, $^1B_1$, $^1B_2$, $^1A_1$, while that corresponding to e^3 is ^2E.

Next considering $\mathbf{D_{6h}}$, we find from Table III that $\pi_{g,u}$ go over into $e^*_{*g,u}$, and $\delta_{g,u}$ into $e^*_{g,u}$. Matching the states of e^{*2}_*,—either g or u,—against those of π^2, and those of e^{*2} against those of δ^2 (which are $^3\Sigma^-_g$, $^1\Gamma_g$, $^1\Sigma^+_g$), one finds that both e^{*2} and e^{*2}_* give rise to the set $^3A_{2g}$, $^1E^*_g$, $^1A_{1g}$. Similarly one finds that $e^{*}{}_g{}^3$ gives $^2E^*_g$, $e^{*}{}_{*g}{}^3$ gives $^2E^*_{*g}$, $e^{*}{}_u{}^3$ gives $^2E^*_u$, $e^{*}{}_{*u}{}^3$ gives $^2E^*_{*u}$.

For the group $\mathbf{O_h}$, method *A* gives the desired results if it is applied twice, reducing one time from $\mathbf{O_h}$ to $\mathbf{D_{4h}}$, then again from $\mathbf{O_h}$, through $\mathbf{T_d}$, to $\mathbf{C_{3v}}$. Reduction to $\mathbf{D_{4h}}$ alone, or to $\mathbf{C_{3v}}$ alone, gives ambiguous results, but when the various sets of states obtained from the two reductions are compared, it is found that there is always one and only one set of states which is common to both.

First we may consider e_g^2 and e_u^2 of $\mathbf{O_h}$. Reducing to $\mathbf{D_{4h}}$, e_g or e_u gives $a_{1g}+b_{1g}$ or $a_{1u}+b_{1u}$ (cf. Table IV). Hence $3_g{}^2$ of $\mathbf{O_h}$ corresponds to $(a_{1g}+b_{1g})^2=a_{1g}{}^2+a_{1g}b_{1g}+b_{1g}{}^2$ of $\mathbf{D_{4h}}$. The groups $a_{1g}{}^2$ and $b_{1g}{}^2$ of $\mathbf{D_{4h}}$ are closed shells (cf. Table I), so each gives $^1A_{1g}$, while $a_{1g}b_{1g}$ gives $^3B_{1g}$ and $^1B_{1g}$; so altogether we have $2^1A_{1g}+{}^3B_{1g}+{}^1B_{1g}$ of $\mathbf{D_{4h}}$. As is easily verified, $e_u{}^2$ of $\mathbf{O_h}$ gives the same result. Now going backward to states of $\mathbf{O_h}$, using Table IV, we find two possibilities: (*a*) $^3A_{2g}+{}^1E_g+{}^1A_{1g}$; (*b*) $^3A_{2g}+{}^1A_{2g}+2^1A_{1g}$. To decide between these, we must use the reduction to $\mathbf{C_{3v}}$.

Reducing to $\mathbf{C_{3v}}$, one first finds (Table IV) that both e_g and e_u of $\mathbf{O_h}$ go into e of $\mathbf{T_d}$ and thence into e of $\mathbf{C_{3v}}$. Hence to find either $e_g{}^2$ or $e_u{}^2$ of $\mathbf{O_h}$, we must find e^2 of $\mathbf{C_{3v}}$. Using the result obtained in a previous paragraph for $\mathbf{D_{6h}}$, that $e^{*}{}_g{}^2=e^{*}{}_u{}^2=e^{*}_{*g}{}^2=e^{*}_{*u}{}^2={}^3A_{2g}+{}^1E^*_g+{}^1A_{1g}$, and reducing to $\mathbf{C_{3v}}$ with the help of Table IV, we find that e^2 of $\mathbf{C_{3v}}={}^3A_2+{}^1E+{}^1A_1$. Going backward from $\mathbf{C_{3v}}$ to $\mathbf{T_d}$ and thence to $\mathbf{O_h}$ by Table 4, we find as possibilities for $e_g{}^2$ and $e_u{}^2$ of $\mathbf{O_h}$ the following: $^3A_{2g}+{}^1T_{2g}$; $^3A_{2g}+{}^1E_g+{}^1A_{1g}$, and six other sets which are obviously out of the question because each contains one or more odd (u) states.

One sees that the correct result is $^3A_{2g}+{}^1E_g+{}^1A_{1g}$, since this and only this is common to the possibilities offered by the reductions to $\mathbf{D_{4h}}$ and to $\mathbf{C_{3v}}$. The result is the same here as that given by Bethe. By similar methods one can show that $e_g{}^3$ gives ^2E_g, $e_u{}^3$ gives ^2E_u, for $\mathbf{O_h}$.

The results given above, and others which have been obtained for $\mathbf{O_h}$ by the method just used, are summarized in Table V. The results for $\mathbf{O_h}$ differ in part from those given by Bethe (cf. his Table XV), in that a decision is made between some alternatives left open by him. (Bethe considered that both alternatives were possible, depending on circumstances, but this seems not to be correct.)

TABLE V. *Resultant states for various numbers of equivalent electrons in molecular orbitals.*

No. Els.	e_g, e_u of **D4h**	e^*_g, e^*_u of **D6h**	e^*_{*g}, e^*_{*u} of **D6h**	e of **C3v**
1	$^2E_{g,\,u}$	$^2E^*_{g,\,u}$	$^2E^*_{*g,\,u}$	^2E
2	$^3A_{2g}+{}^1B_{1g}+{}^1B_{2g}+{}^1A_{1g}$	$^3A_{2g}+{}^1E^*_g+{}^1A_{1g}$	$^3A_{2g}+{}^1E^*_g+{}^1A_{1g}$	$^3A_2+{}^1E+{}^1A_1$
3	$^2E_{g,\,u}$	$^2E^*_{g,\,u}$	$^2E^*_{*g,\,u}$	^2E
4	$^1A_{1g}$	$^1A_{1g}$	$^1A_{1g}$	$^1A_1$

	e_g, e_u of **Oh**	t_{1g}, t_{1u} of **Oh**	t_{2g}, t_{2u} of **Oh**
1	$^2E_{g,\,u}$	$^2T_{1g,\,u}$	$^2T_{2g,\,u}$
2	$^3A_{2g}+{}^1E_g+{}^1A_{1g}$	$^3T_{1g}+{}^1A_{1g}+{}^1E_g+{}^1T_{2g}$	$^3T_{1g}+{}^1A_{1g}+{}^1E_g+{}^1T_{2g}$
3	$^2E_{g,\,u}$	$^1A_{1g,\,u}+{}^2E_{g,\,u}+{}^2T_{1g,\,u}+{}^2T_{2g,\,u}$	$^1A_{2g,\,u}+{}^2E_{g,\,u}+{}^2T_{1g,\,u}+{}^2T_{2g,\,u}$
4	$^1A_{1g}$	Same as for two electrons	
5		Same as for one electron	
6		$^1A_{1g}$	$^1A_{1g}$

APPLICATION TO CH_2 AND C_2H_4

8. The molecules CH_2 and C_2H_4

In III of this series, the formation of C_2H_4 from $2CH_2$ was discussed. Several statements were made there, without proof, whose justification depends on the results of the present paper. In order to give this justification and also to illustrate the methods described above, the electronic structures of CH_2 and C_2H_4 will be considered again now. The following discussion and that in III supplement each other, and should be read together.

Applications to other molecules will be given in later papers. The basis for a number of conclusions stated in I of this series can, however, now easily be found by the reader, if he wishes, in the Tables I–IV given above.

8a. The molecule CH_2. The CH_2 molecule, assuming it to have the form of an isosceles triangle (cf. III), has the symmetry of the point group **C2v** (cf. Table I). Electronic configurations of CH_2 were given in III in terms of molecular orbitals called $[s]$, $[x]$, $[y]$, $[z]$, and respectively capable of being approximated by linear combinations of $2s$, $2p_x$, $2p_y$, $2p_z$ orbitals of the carbon atom with hydrogen $1s$ orbitals, hereafter called α and β. With the choice of x, y, z axes described in III it will be found, on testing their behavior under the symmetry operations of **C2v**, that carbon $2s$, $2p_x$, $2p_y$, $2p_z$ respectively belong to the representations a_1, b_1, b_2, a_1 of **C2v**. The linear combinations with α and β, formed in such a way that they still belong to these same representations, are

$$\left.\begin{aligned} &[s]=a(2s)+b(\alpha+\beta)+c(2p_z); \quad [x]=2p_x.\\ &[y]=a'(2p_y)+b'(\alpha-\beta).\\ &[z]=a''(2p_z)+b''(\alpha+\beta)+c''(2s). \end{aligned}\right\} \tag{8}$$

The fact that $2s$ and $2p_z$ of carbon belong to the same representation allows and requires them to hybridize somewhat with each other when CH_2 is formed. Since α and β by themselves are not representations of **C2v**, their hybridization with the carbon orbitals, necessary to obtain bonding orbitals in CH_2, can take place freely provided the coefficients of α and β are so related that the resulting hybrids belong to representations of **C2v**. In the case of $[x]$, these coefficients are zero because $2p_x$ belongs to a representation b_1 which demands that the plane of the three nuclei shall be a nodal plane.

The fact that the electron configuration $1s^2[s]^2[y]^2[z]^2$ of Eq. (1) of III gives a $^1A_1$ state (called $^1\Gamma_1$ in the notation of III) is an illustration of the rule that a set of closed shells always gives the identical representation (cf. section 7). On applying the rules of section 7, one finds that $\cdots[z][x]$ in Eq. (1) of III, which is of the type $\cdots a_1b_1$, gives a $^3B_1$ and a $^1B_1$ state (called $^3\Gamma_3$ and $^1\Gamma_3$ in III), of which we may reasonably expect the $^3B_1$ to have the lower energy.

8b. Formation of C_2H_4. The normal plane form of C_2H_4 (rotation angle 0° or 180° in Fig. 2 of III) has the symmetry **Vh**, the perp. form (rotation angle 90° or 270°) the symmetry **Vd**, while all intermediate forms belong to **V**: cf. Table I. In order to make the notation used in III conform to the revised notation of Table I, the following changes must be made: *for plane*

C_2H_4 in III (Eqs. (2, 3, 5) and elsewhere), *read* $^1A_{1g}$, $^3B_{1u}$, $^1B_{1u}$ *everywhere instead of* $^1\Gamma_{1g}$, $^3\Gamma_{4u}$, $^1\Gamma_{4u}$; *for perp.* C_2H_4 in III (Eqs. (6, 7), Fig. 1, and elsewhere), *read* $^3A_2$, $^1B_1$, $^1B_2$, $^1A_1$ *instead of* $^3\Gamma_3$, $^1\Gamma_2$, $^1\Gamma_4$, and $^1\Gamma_1$.

The orbitals $[x+x]$, and so on, of plane C_2H_4 (cf. III) have been so constructed from $[x]$, and so on, of CH_2 that they conform to representations of $\mathbf{V_h}$. As the reader can easily verify by testing the behavior of each under the symmetry operations of $\mathbf{V_h}$ (cf. Table I), the orbitals $[x+x]$, $[x-x]$, $[y+y]$, $[y-y]$, $[z+z]$ of plane C_2H_4 belong respectively to the representations b_{3u}, b_{2g}, b_{2u}, b_{3g}, a_{1g}. Any electron configuration consisting of closed shells, e.g., that in Eq. (2) or (3) of III, gives a $^1A_{1g}$ state. By applying the rule given in section 7, it is found that $\cdots[x+x][x-x]$, which is of the type $\cdots b_{3u}b_{2g}$, gives a $^3B_{1u}$ and a $^1B_{1u}$ state ($^3\Gamma_{4u}$ and $^1\Gamma_{4u}$ in the notation of III, cf. Eq. (5)).

Next we may consider perp. C_2H_4 (symmetry $\mathbf{V_d}$), and its formation from $2CH_2$, each in the state $\cdots[z][x]$, $^3B_1$ with their planes at right angles. The axes appropriate to $\mathbf{V_d}$ then are an x and a y axis whose directions make 45° angles with the x and y directions of the two CH_2, and a z axis coincident with the z axes of both. To get stable forms of perp. C_2H_4, one forms the bonding pair $[z+z]^2$ from the two $[z]$ electrons of $2CH_2$. The orbital $[z+z]$ of perp. C_2H_4, although constructed in zeroth approximation from two $[z]$ each as in Eq. (8), is not identical with $[z+z]$ of plane C_2H_4. It belongs to representation a_1 of $\mathbf{V_d}$.

Let us now denote by $[x]_A$ and $[x]_B$ the $[x]$ orbitals of the two CH_2, whose x axes, it should be remembered, are at right angles. On testing the effect of the symmetry operations of $\mathbf{V_d}$ on $[x]_A$ and $[x]_B$, one finds changes of the type

$$\begin{cases} [x]_A \rightarrow c_{AA}[x]_A + c_{AB}[x]_B \\ [x]_B \rightarrow c_{BA}[x]_A + c_{BB}[x]_B. \end{cases}$$

By writing down the sums $c_{AA}+c_{BB}$ and regarding them as characters (cf. section 4), one finds that the *pair* $[x]_A$, $[x]_B$ gives exactly the set of characters belonging to the two-dimensional representation e of $\mathbf{V_d}$. This shows that the CH_2-radical orbitals $[x]_A$, $[x]_B$, degenerate for $2CH_2$, remain so if perp. C_2H_4 is formed, and constitute suitable zeroth approximations for molecular orbitals of perp. C_2H_4.

Exactly the same situation holds for the pair of CH_2-radical orbitals $[y]_A$, $[y]_B$, and therefore the four electrons $[y]_A^2[y]_B^2$ of $2CH_2$, in spite of the fact that each of the two pairs already forms a closed shell of CH_2, all belong in perp. C_2H_4 to a single degenerate type of C_2H_4-molecule orbitals belonging to representation e, and together form a larger closed shell of type e^4. This is true even though (or even if) these electrons are not shared in any real sense by the two CH_2 radicals.

In III (cf. especially Eqs. (6, 7) and reference 6) the types $e\{[y]_B, [y]_A\}$ and $e\{[x]_A, [x]_B\}$ were called $[\pi]_y$ and $[\pi]_x$ because the relation between $[y]_B$ and $[y]_A$, or between $[x]_A$ and $[x]_B$, is rather similar to that between the two orbitals which belong to a representation π of a diatomic molecule. (One should not attach too much significance to this notation, however.) The fact that both the types $\{[x]_A, [x]_B\}$ and $\{[y]_B, [y]_A\}$ belong to the same representation e shows that there must be more or less hybridization between them. Possible consequences of some importance are discussed in section 8*e*. Until then they will for simplicity be treated as independent.

In the same way as for any degenerate pair of orbitals, one may replace $[x]_A$, $[x]_B$ of perp. C_2H_4 by any two mutually orthogonal linear combinations, for example by *const.* $\{[x]_A + [x]_B\}$ and *const.* $\{[x]_A - [x]_B\}$. (Similarly with $[y]_B$, $[y]_A$.) This is instructive when used in making comparisons with $[x+x]$ and $[x-x]$ of plane C_2H_4. (One should recall that $[x+x]$ is just an abbreviation for *const.* $\{[x]_A+[x]_B\}$.)

In plane C_2H_4, $[x+x]$ and $[x-x]$ are far apart in energy and are respectively strongly bonding and strongly antibonding, while in perp. C_2H_4 they belong to a single degenerate representation and are therefore rather obviously essentially nonbonding, as are also of course $[y+y]$ and $[y-y]$ of perp. C_2H_4 (cf. also III, beginning of paragraph containing Eq. (6)). Between plane and perp. C_2H_4 lies a continuous set of intermediate cases. Everywhere except for perp. C_2H_4, it is necessary to use orbitals of the types $[x+x]$ and $[x-x]$, which then belong to different nondegenerate representations of the

appropriate point group. Just for the angles 90° and 270°, $[x+x]$ and $[x-x]$ become degenerate, and can if desired be replaced by $[x]_A$, $[x]_B$.

It is of interest to note here how the unshared-electron notation $[x][x]$ automatically becomes appropriate as the rotation angle approaches 90°, corresponding to the gradual breaking of the second bond of the double bond by twisting it. [In the case of $[y]^2[y]^2$ (cf. Eqs. (2, 6, 7) of III), the unshared-electron (CH_2-radical) notation is used for all angles, but for a different reason, namely that we have arbitrarily agreed to use it for electrons which are essentially unshared.] For perp. C_2H_4, both $[x]$ and $[y]$ orbitals may be considered as CH_2-radical or as C_2H_4-molecule orbitals with equal appropriateness.

8c. Electronic states, correlations, selection rules for C_2H_4. The problem of determining the possible electron states corresponding to an electron configuration e^2 (in particular, $[\pi]_x^2$ of $\mathbf{V_d}$) has been solved in section 7. The states are $^3A_2$, $^1B_1$, $^1B_2$, $^1A_1$ as stated (except for changed notation) in III (cf. Fig. 1).

Next it may be well to justify the correlations shown in Fig. 1 between the states of plane and perp. C_2H_4. This is readily done by using Table IV to see how the representations of $\mathbf{V_d}$ (perp. C_2H_4) and of $\mathbf{V_h}$ (plane C_2H_4) go over into those of $\mathbf{V}$ (intermediate angles). The results are: A_1 or B_1 of $\mathbf{V_d}$ can go (by way of A_1 of $\mathbf{V}$) into either A_{1g} or A_{1u} of $\mathbf{V_h}$, A_2 or B_2 of $\mathbf{V_d}$ (by way of B_1 of $\mathbf{V}$) into B_{1g} or B_{1u} of $\mathbf{V_h}$, while E of $\mathbf{V_d}$ splits (into B_2+B_3 of $\mathbf{V}$, which go) into B_{2g} or B_{2u} plus B_{3g} or B_{3u} of $\mathbf{V_h}$. Also, singlet→singlet, triplet→triplet. After changing the notation, Fig. 1 of III will be found consistent with these rules. One might, however, raise the question whether an adiabatic correlation scheme is appropriate to the problem considered in III (absorption of ultraviolet light followed by spontaneous relative rotation of the two halves of C_2H_4), since for such rotations the wave function cannot very well be separated into an electronic and a rotational part. Lack of separability might change the restrictions given above, except the singlet→singlet . . . rule, but, as it happens, could not effectively alter the correlations shown in Fig. 1 and so would not lead to any change in the conclusions reached in III.

The fact that a transition $^1A_{1g}\rightarrow{}^1B_{1u}$ of $\mathbf{V_h}$, identified in III (except for change of notation) with the ultraviolet absorption of C_2H_4, is allowed by the selection rules can now be verified by the method of Eq. (7); and it is seen that the electric moment is parallel to the z axis.

8d. Wave functions (ψ) and dissociation of C_2H_4. The various states of C_2H_4 have so far been described in terms of electron configurations, i.e., sets of (atomic and) molecular orbitals, but expressions have not been given for the wave functions of the molecule (cf. sections 2, 2a, 3b). It is of interest to see how approximate ψ's can be constructed (a) with C_2H_4-molecule orbitals for the valence or shared electrons, (b) with CH_2-radical orbitals as one would use atomic orbitals in the method of atomic orbitals. (The reader should refer at this point to the last two paragraphs of section 2.)

Using C_2H_4-molecule orbitals, one has for the normal state of plane C_2H_4

$$\psi = N \begin{vmatrix} [x+x]\alpha(1) & [x+x]\alpha(2) & \cdots(3) & \cdots(4) & & \\ [x+x]\beta(1) & \cdots\beta(2) & (3) & (4) & & \\ [z+z]\alpha(1) & (2) & (3) & (4) & \text{etc.} & : {}^1A_{1g} \\ [z+z]\beta(1) & (2) & (3) & (4) & & \\ & \text{etc.} & & & & \end{vmatrix} \tag{9}$$

Here "etc." refers to electrons 5 to 16, which are all in CH_2-radical or C-atom closed shells (cf. discussion of H_2O following Eq. (2)). The two excited states $^3B_{1u}$ and $^1B_{1u}$ are given, for $M_S=0$, by

$$\psi = N \begin{vmatrix} [x+x]\alpha(1) & \cdots(2) & & \\ [x-x]\beta(1) & \cdots(2) & \text{etc.} & \\ \text{etc. as before} & & & \end{vmatrix} \pm N \begin{vmatrix} [x+x]\beta(1) & \cdots(2) & & \\ [x-x]\alpha(1) & \cdots(2) & \text{etc.} & \\ \text{etc. as before} & & & \end{vmatrix} : \begin{cases} {}^3B_{1u} \\ {}^1B_{1u} \end{cases} \tag{10}$$

Another excited state is the following:

$$\psi = N \begin{vmatrix} [x-x]\alpha(1) & \cdots(2) & \\ [x-x]\beta(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} : {}^1A_{1g} \qquad (9')$$

The approximations (9) and (9′), which belong to the same representation, could both be improved by forming linear combinations whereby a little of (9′) is admixed with (9) and *vice versa*. That the expressions given for ψ in (9), (10), and (9′) actually belong to the representations A_{1g} and B_{1u} of $\mathbf{V_h}$ can be verified by testing the behavior of each under the symmetry operations of $\mathbf{V_h}$. The spin character of each can also be verified easily.

Expressions (9), (10), and (9′) apply also to forms of C_2H_4 intermediate between the plane and perp. forms, the states then being ${}^1A_1$ of $\mathbf{V}$ for (9) and (9′), ${}^3B_1$, ${}^1B_1$ for (10). Expression (10) still holds even for perp. C_2H_4, and the two states then prove to have exactly the symmetry properties of ${}^3A_2$ and ${}^1B_2$ of $\mathbf{V_d}$. Although expressions (9) and (9′) both conform to ${}^1A_1$ of $\mathbf{V}$, neither conforms to any representation of $\mathbf{V_d}$. Instead one must form the two linear combinations

$$\text{(Perp. } C_2H_4\text{)} \quad \psi = N \begin{vmatrix} [x+x]\alpha(1) & \cdots(2) & \\ [x+x]\beta(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} \mp N \begin{vmatrix} [x-x]\alpha(1) & \cdots(2) & \\ [x-x]\beta(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} : \begin{cases} {}^1B_1 \\ {}^1A_1 \end{cases} \qquad (9'')$$

Evidently the two types (9) and (9′) which differ greatly in energy and are slightly admixed for plane C_2H_4 must admix more and more as one goes from plane to perp. C_2H_4, until in the latter they are mixed in equal proportions (Eq. (9″)). This is connected with the fact, noted in an earlier paragraph, that the orbitals $[x+x]$ and $[x-x]$, although differing greatly in energy for plane C_2H_4, become degenerate for perp. C_2H_4, so that (9) and (9′) converge toward the same energy as one approaches perp. C_2H_4. The two energy curves starting approximately from (9) and (9′) of plane C_2H_4 avoid coming together, however, by interacting strongly to give the two states ${}^1A_1$ and ${}^1B_1$ of (9″). These states, together with ${}^3A_2$ and ${}^1B_2$, whose ψ's are given by Eq. (10), are of just the four types which, as we have seen in an earlier paragraph, are expected according to the group theory method when we have e^2 of $\mathbf{V_d}$, the type e here being represented by the two forms $[x+x]$, $[x-x]$.

Even more interesting results for perp. C_2H_4 are obtained by building up the ψ's using the pair of perp. C_2H_4 orbitals $[x]_A$, $[x]_B$ instead of the equivalent forms $[x+x]$, $[x-x]$. In terms of $[x]_A$, $[x]_B$,—which, it may be recalled, can also be regarded equally well as orbitals of CH_2,—the four states of perp. C_2H_4 just discussed appear as

$$\psi = N \begin{vmatrix} [x]_A\alpha(1) & \cdots(2) & \\ [x]_B\beta(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} \pm N \begin{vmatrix} [x]_A\beta(1) & \cdots(2) & \\ [x]_B\alpha(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} : \begin{cases} {}^3A_2 \\ {}^1B_1 \end{cases} \qquad (11)$$

$$\psi = N \begin{vmatrix} [x]_A\alpha(1) & \cdots(2) & \\ [x]_A\beta(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} \mp N \begin{vmatrix} [x]_B\alpha(1) & \cdots(2) & \\ [x]_B\beta(1) & \cdots(2) & \text{etc.} \\ \text{etc.} & & \end{vmatrix} : \begin{cases} {}^1B_2 \\ {}^1A_1 \end{cases} \qquad (12)$$

By multiplying out each of the four cases given by Eqs. (11, 12), one finds that each is identical with one of those obtained by multiplying out the expressions given by Eqs. (9″, 10). (Nothing of interest is lost if all the "etc." parts are dropped before multiplying.)

The forms of Eqs. (11) and (12) show that ${}^3A_2$ and ${}^1B_1$ tend to dissociate so as to leave one $[x]$ electron on each CH_2, but ${}^1B_2$ and ${}^1A_1$ so as to leave both on one CH_2, corresponding to $CH_2^+ + CH_2^-$. Of course the actual adiabatic dissociation processes would be mostly different.

The most probable adiabatic correlations are shown in Fig. 1 of III.

Consideration of Eqs. (9″–12) and of the integrals representing interactions between electrons in $[x+x]$ and $[x-x]$ orbitals indicates that the four states $^3A_2$, $^1B_1$, $^1B_2$, $^1A_1$ of perp. C_2H_4 lie within a moderate energy range. In this connection it should not be forgotten that the two parts of the molecule are always being held together strongly by the $[z+z]^2$ bond. Definite predictions can, however, hardly be made without careful study. The arrangement given in Fig. 1 of III seems plausible.

It will now be instructive to consider the formation of plane and perp. C_2H_4 by the method of atomic orbitals treating each CH_2 like an atom (cf. end of section 2). For simplicity we may disregard the $[z]$ electrons of CH_2, since their behavior is essentially the same as that of the 1*s* hydrogen electrons in the formation of H_2. The latter is to a considerable extent also true of the $[x]$ electrons of CH_2. In fact Eqs. (11) and (12) above, if we regard $[x]_A$ and $[x]_B$ as CH_2 and not as C_2H_4 orbitals, correspond exactly in form to the ψ's for the four states of H_2 ($^1\Sigma_g^+$, $^3\Sigma_u^+$, $^1\Sigma_u^+$, $^1\Sigma_g^+$) derivable from $2H(1s)$ and from $H+H(1s^2)$. Eqs. (11) and (12) really apply not only for perp. C_2H_4 but also for plane and intermediate nuclear configurations, where they are the correct forms for the atomic orbital method. The forms which belong to $^3A_2$, $^1B_2$, $^3B_2$, $^1A_1$ for perp. C_2H_4 in Eqs. (11, 12) belong respectively to $^3B_1$, $^1A_1$, $^1B_1$, $^1A_1$ for intermediate and to $^3B_{1u}$, $^1A_{1g}$, $^1B_{1u}$, $^1A_{1g}$ for plane C_2H_4.

Comparing Eqs. (9, 10, 9′) with (11, 12), for plane C_2H_4, the relations and differences are exactly analogous to those between the methods of molecular and atomic orbitals as applied to the four states of H_2 mentioned above. On multiplying out the various expressions, those for the $^3B_{1u}$ and $^1B_{1u}$ states as given by the two methods are identical, while those for the two $^1A_{1g}$ states differ characteristically, but can be brought into agreement by abandoning pure electron configurations (cf. section 2) and taking suitable admixtures of the two $^1A_{1g}$ forms in each case (cf. II, section 13, after dropping the spins from the present equations). For perp. C_2H_4, the two methods become identical in all respects. All these relations are true, however, only provided we omit all but the $[x]$ electrons of CH_2 from consideration.

8e. Partial persistence of second bond in perp. C_2H_4. In an earlier paragraph it was mentioned that there must be more or less hybridization between the two *e* orbital types $[\pi]_x=\{[x]_A, [x]_B\}$ and $[\pi]_y=\{[y]_B, [y]_A\}$. Of these two types, it should be noted $[\pi]_y$ is presumably decidedly the lower in energy. The two resulting hybrid *e* types would be of the forms

$$q=\{a[y]_A+b[x]_B\},\ \{a[y]_B+b[x]_A\},\quad \text{and}$$

$$r=\{a[x]_B-b[y]_A\},\ \{a[x]_A-b[y]_B\}. \qquad (13)$$

Complete hybridization would make $a=b$, and would make the two types closely similar to the types π and π^* of O_2 (described as $(\pi+\pi)$ and $(\pi-\pi)$ in III). They would differ in zeroth approximation from π and π^* only because the $[y]$ orbitals contain contributions from hydrogen 1*s* and are C−H bonding (cf. Eq. (8) above).

Actually $a>b$ must hold, but it is reasonable to suppose that $a\gg b$ is not true. Then, as is obvious from its form, the lower-energy type *q*, which is the more closely related to $[\pi]_y$, has more or less C−C bonding power while type *r* has more or less C−C anti-bonding power. Since, corresponding to $[\pi]_y{}^4[\pi]_x{}^2$ for the case of no hybridization, one has q^4r^2, the result is that hybridization tends to produce a net C−C bonding effect like the O−O bonding effect of $\pi^4\pi^{*2}$ in O_2. It appears, then, that the double bond in perp. C_2H_4 is intermediate in character between the model given in III and the double bond $(\sigma^2\pi^4\pi^{*2})$ of O_2.

We now see that a 90° rotation of the two parts of a C_2H_4 molecule after all does not entirely destroy the second bond of the double bond, so that the energy difference between the normal state of plane C_2H_4 and the lowest states of perp. C_2H_4 should be less than in Fig. 1 of III. This would make the energy differences between the excited plane states and the perp. states correspondingly greater, and increase the probability of the correctness of the interpretation given in III of certain photochemical experiments.

The change in Fig. 1 just mentioned also brings it into better agreement with calculations from chemical data (cf. III, last sentence before

section on *Interpretation of Photochemical Experiments*), according to which the "energy of activation" required to pass over the hill or hills of energy near 90° between *cis* and *trans* forms of ethylene derivatives is much smaller (of the order of one volt) than in Fig. 1 of III. It should be remarked, however, that it is rather uncertain how closely the chemically calculated energy of activation may be expected to correspond to the energy maximum between *cis* and *trans*.

It should further be noticed that if by hybridization the group q^1r^2 has acquired some C−C bonding power, this is partly at the expense of the C−H bonding power of the $[y]$ orbitals. One can see this by, for example, observing (1) that the configuration q^1r^2 with complete hybridization ($a=b$ in Eqs. (13)) corresponds to the occurrence in $2CH_2$ of only three of the C−H bonding orbitals $[y]$ and three of the C−H nonbonding orbitals $[x]$, as against four and two respectively if there is no hybridization; but noticing at the same time (2) that complete hybridization would result in a net gain of two C−C bonding orbitals, so that on the whole the effect of hybridization could well be an appreciable lowering of the energy of the states of perp. C_2H_4 as compared with Fig. 1. That the energy decrease would be fairly large has not here been proved theoretically, but the empirical evidence on activation energies suggests that this may be the case.

A matter not yet explained is the method by which conclusions were reached as to the relative energies of binding of various molecular orbitals. (The conclusions themselves are implicit in the electron configuration formulas given in III, since the orbitals are always written in what seems their most likely order of binding energy.) Details will be postponed, but in brief, the principle used was mainly this: molecular orbitals which are strongly bonding are relatively concentrated in a relatively strong field of force, and so, other things being equal, have lower energy than those which are less strongly bonding.

Everything stated in III concerning C_2H_4 and its formation from $2CH_2$ has now been justified or improved on, except the matter of the rules for the adiabatic correlation of C_2H_4 with $2CH_2$ on dissociation. Discussion of this problem, and of the ways in which other double-bonded compounds differ from C_2H_4, will be reserved until later.

Note added in proof: In a forthcoming paper in the *Zeits. f. Physik*, dealing primarily with vibrational states of molecules, L. Tisza gives among other interesting results the representations of all possible point groups, including groups with 5-, 7-, 8-, . . . fold axes. In another forthcoming paper, E. Teller and G. Herzberg discuss in detail some of the consequences of the Franck-Condon principle, and of the interaction between electronic states and vibration, for selection rules and intensity relations in electronic bands of polyatomic molecules.[18, 19]

[18] The writer is indebted to Dr. E. Teller in Göttingen for the opportunity of seeing the manuscripts of these papers.

[19] For earlier applications of the Franck-Condon principle to this problem, cf. G. Herzberg, Trans. Faraday Soc. **27**, 378 (1931); H. C. Urey and H. Johnston, Phys. Rev. **38**, 2131 (1931).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Chemical Intensification of X-Ray Spectrograms

The use of chemical intensifying and toning baths in pictorial photography is a common practice, but such treatment of the negative has found little or no application in the field of spectroscopic photography. The reason is evident: the spectroscopist hesitates to tamper with a developed image on which he desires to make quantitative measurements. If the spectrogram is to be used in qualitative analysis, however, such an objection obviously no longer holds.

Since many of the x-ray spectrograms for the purpose of qualitative chemical analysis yield faint lines even after unduly long exposures, a means was sought of intensifying the faint lines of the developed image. A group of mercury intensifiers were tried first, but gave poor results; the intensification was uniform with little increase in contrast.[1] Much better results were obtained with the well-known uranium baths as far as contrast and detail were concerned. Both visual and photographic densities were increased, and especially in the case of faint lines; lines of doubtful visibility were made to show up with certainty after intensification.[2] Nietz and Huse, in an investigation of the sensitometry of a large number of intensifiers, found that the uranium treatment gave 200–250 percent increase in photographic density, this being by far the highest found of all the baths used.[3]

The procedure used for the x-ray plates is the same as that recommended in pictorial practice except that it is unnecessary to wet the plates first. The red-brown color of the treated plate acts as a fairly effective screen for the actinic rays. Thus, when printing from the intensified negative, it is necessary to expose the print four to five times longer than if the negative were untreated, in order to obtain a background which is of approximately the same degree of blackness as that of a print from the original untreated negative.

Sensitometrically, lines of the negative after treatment were found to be 2.0–2.5 times as dense as the lines of the original negative. It was first thought that this value was incorrect because of the fact that the caesium cell used in the photometer has the peak of its sensitivity in the red region. Consequently, prints were made from the negative, before and after intensification, on plates identical in type with the original negative. See Fig. 1. The measurement of

FIG. 1. (a) Before intensification. (b) After intensification.

these printed plates gave about the same results as before, the densities of the lines of the print made from the treated negative being 2.0–2.5 times those of the lines of the print from the original.

The appended microphotometer records were prepared from prints of the $K\alpha$ lines of nickel.

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January 2, 1933.

[1] C. B. Neblette, *Photography, Principles and Practice*, pp. 352–363, 2nd Edition, 1932, D. Van Nostrand, N. Y.

[2] Selle, Phot. Archiv. 326 and 393 (1865). Eder, Handb. d. Photographie **2**, 272 (1897). Sedlaczek, Phot. Ind. 234, 1924.

[3] Nietz and Huse, Photographic Jour. **58**, 81 (1918). J. Franklin Inst., March, 1918.

Perturbation Theory and Electron Scattering

So far as the writer is aware the literature on the quantum mechanics of electron scattering does not contain a treatment analogous to the classical derivation of Rutherford's formula in which the theorems of conservation of angular momenta are paramount. This can easily be supplied, and although it does not furnish the scattering formula in a useful form, nevertheless it seems of some interest for conceptual reasons. The analysis can be based on the fact that if one uses as auxiliary dynamical variables a set of independent commuting operators which, with the energy, are just equal in number to the number of degrees of freedom of the system, and if the perturbation energy commutes with one or more of them (not including the energy, of course) then the states of the system can be divided into two or more groups between which the perturbation causes no interaction, each group corre-

sponding to definite values of those quantities which commute with the total energy operator and so remain quantized. Simple applications of this result have been used many times in atomic and molecular problems, and the general theorem is evident.

Applying this to the scattering of electrons by a bare nucleus we see that the square of the angular momentum and the component on one axis (say the z) are quantized. The impacting electrons are represented by a plane wave $(2\pi m/hk)^{\frac{1}{2}}e^{ikz}$ normalized to unit current density. Expanding this into states corresponding to quantized M_z and M^2

$$(2\pi m/hk)^{\frac{1}{2}}e^{ikz}=-i\sum_{l=0}^{\infty}[2\pi^2m(2l+1)/hk](\mathbf{r}\,|\,kl0),$$

where

$$(\mathbf{r}\,|\,klm)=i^{l+1}(2\pi/kr)^{\frac{1}{2}}J_{l+\frac{1}{2}}(kr)_{Pl}{}^{|m|}(\cos\theta)e^{im\varphi}.$$

Writing generally

$$\psi=\sum_l\sum_m c_{lm}(t)(\mathbf{r}\,|\,klm)e^{-i(hk^2/4\pi m)t}$$

we find for the exact solution of the perturbation equations

$$c_{lm}(t)=\delta_{m,0}[-i(2\pi^2m(2l+1)/hk)^{\frac{1}{2}}]e^{-i(2\pi/h)(klm|H_1|klm)t},$$

where

$$(klm\,|\,H_1\,|\,klm)=[\int|(\mathbf{r}\,|\,klm)|^2H_1d\mathbf{r}]/[\int|(\mathbf{r}\,|\,klm)|^2d\mathbf{r}].$$

We have now only to expand $(\mathbf{r}\,|\,kl0)$ into plane waves with normals distinguished by the angles Θ, Φ by the expression

$$(\mathbf{r}\,|\,kl0)=\frac{i}{(2\pi)^{\frac{3}{2}}(l+\frac{1}{2})^{\frac{1}{2}}}\int_0^{2\pi}d\Phi\int_0^{\pi}\sin\Theta d\Theta \times P_l(\cos\Theta)e^{ikr|\sin\theta\sin\Theta\cos(\varphi-\Phi)+\cos\theta\cos\Theta|}.$$

This yields at once a probability of scattering for a time interval t in the solid angle $\sin\Theta d\Theta d\Phi$ proportional to

$$k|\sum_{l=0}^{\infty}[e^{-i(2\pi/h)(kl0|H_1|kl0)t}-1]P_l(\cos\Theta)|^2\sin\Theta d\Theta d\Phi.$$

This expression can be easily generalized to take account of inelastic scattering collisions. An approximate expression is obtained by expanding the exponential, retaining the first two terms only, but the resulting formula is formally improper for an inverse square field, as indeed it should be since the Rutherford scattering expression, which it should represent, cannot be expanded in a Legendre sum. The value of the analysis is to point out how one can treat the scattering of electrons of given angular momentum in the incident beam in a manner independently of the others.

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January 25, 1933.

The Disintegration of Boron by Swiftly Moving Protons

With the apparatus used by Lawrence, Livingston and White,[1] and Henderson[2] in experiments on the disintegration of lithium, we have studied the disintegration of boron, and have obtained surprisingly similar results.

High-speed protons, striking a boron oxide target gave rise to radiations which passed through a mica window (stopping power 2.7 cm of air) into the chamber of a Geiger point counter. Cockcroft and Walton[3] have established that the radiation given off by boron under the circumstances consists of alpha-particles, and in our experiments it is safe to assume that the observed number of counts per minute is closely equal to the number of alpha-particles passing through the mica window into the counting chamber.

Our experimental observations are shown plotted as circles in the accompanying figure. The ordinates represent the number of counts per minute per milli-microampere of bombarding protons having the energies in kilovolt-electrons given by the abscissas. In addition to the full line curve, which represents closely the boron observations, there is plotted the dotted line curve which represents the corresponding observations of Henderson on lithium.

We were somewhat surprised to find that the yield of alpha-particles from boron for voltages above 500,000 is very nearly the same as from lithium. We rather expected that because of the higher atomic number of boron, correspondingly higher voltages would be required to produce the same disintegration yield.

Since the completion of these experiments we have seen the letter to *Nature* of Cockcroft and Walton[4] reporting new work in which they find a wide distribution of ranges of the alpha-particles from boron, making it evident that our observed yields would have been even much greater had we used a thinner mica window on the counting

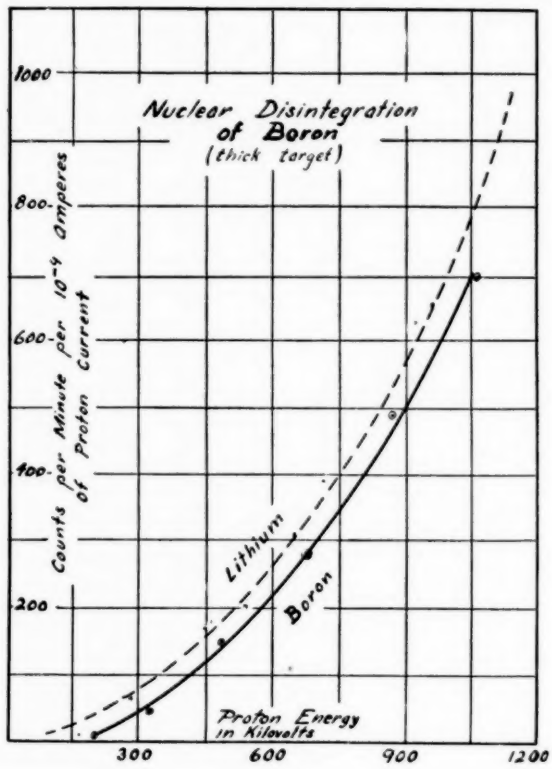

FIG. 1.

chamber. On one occasion we inserted an additional sheet of mica in the path of the disintegrating alpha-particles and found that about one in seven has a range in excess of 4.3 cm. (See Fig. 1.)

The fact that the disintegration of boron varies with proton voltage in the same way as in the case of lithium, is particularly interesting. Beyond 400 kilovolts, as has been pointed out by Henderson, the entire increase in the rate of disintegration is accounted for by the greater distance the protons travel in the boron. In other words, the observations for both lithium and boron indicate that the effective collision cross section for disintegration does not increase perceptibly with the speed of the proton beyond four or five hundred thousand volts.

We are continuing the experiments with other elements. It will be interesting to see if any of higher atomic number, particularly those of the $4n+3$ type, have an effective collision cross section for disintegration that attains a constant value at such low voltages.

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January 27, 1933.

[1] E. O. Lawrence, M. G. White, M. S. Livingston, Phys. Rev. **42**, 150, 151 (1932).
[2] M. C. Henderson, Phys. Rev. **43**, 98 (1933).
[3] J. D. Cockcroft and E. T. S. Walton, Proc. Roy. Soc. **A137**, 229–242 (1932).
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Occurrence of $CuAl_2$ in Duralumin

The presence of $CuAl_2$ in the duralumin type of aluminum alloys has been detected in the past both micrographically[1] and by x-ray methods,[2, 3, 4] the x-ray diffraction method being most sensitive and giving unambiguous results while the interpretation of micrographic evidence is often difficult.

Previously, $CuAl_2$ has been found in these alloys (about 4 percent Cu) only in very small quantities after very long accurately controlled heat treatment following quenching.

During an x-ray investigation of the condition of duralumin aircraft propeller blades very large quantities of $CuAl_2$ were found by x-ray diffraction and photomicrographs to exist in certain portions of an old blade that had been in use for twice the number of flying hours of the average blade. Throughout the major part of the blade very little $CuAl_2$ could be found and this only in the outermost fibers. However, an examination of the circular cross section just outside of the position of the steel hub clamp showed that large quantities of this intermetallic compound had precipitated from the solid solution. This region of precipitation extended throughout the entire section, the amount of $CuAl_2$ decreasing from the outside surface toward the geometrical center of the section. Largest amounts of the compound were found in the region of the neutral plane.

The amounts of $CuAl_2$ found in the hub section are much larger than could have been caused by any known type of heat treatment for ordinary lengths of time[5] and it is thought probable that the peculiar combination of forces existent in propeller blades is the cause of this abnormal condition, i.e., lattice strain, fatigue and high-frequency vibration and a combination of these with particular types of heat treatment and a time factor hasten the precipitation of the compounds. The discovery of the causes and the allocation of this excessive precipitation of $CuAl_2$ should be of vital importance in the development of more satisfactory manufacturing methods and of a more stable alloy.

The results of a more detailed study now being made of this and other blades as well as of the specific effects of repeated stress, lattice strain and high-frequency vibration on the precipitation of intermetallic compounds from metastable solid solutions will be published at a later date.

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February 1, 1933.

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The Infrared Spectrum and the Molecular Structure of Ozone and Sulfur Dioxide

The writers have been interested in the fine experimental work on the infrared absorption spectrum of ozone by Gerhard,[1] but they cannot agree with his conclusions as to the structure of the ozone molecule, nor with the conclusions of Bailey, Cassie and Angus[2] in regard to that of sulfur dioxide. These authors have postulated for the molecules in question structures in the shape of an isosceles triangle with an apex angle less than 60°, but this seems very unlikely from several points of view.

In the first place, since nearness of approach of two adjacent atoms is one criterion for a chemical bond, and since the distance of approach is a measure of the strength of the bond, the structure mentioned would require two atoms strongly bound to each other (in sulfur dioxide, the two oxygen atoms) and the third less strongly bound to both of these two, or in other words, a ring structure. In ozone a ring structure is unlikely unless it is completely symmetrical, which it clearly cannot be since all three

fundamental oscillations are active, and in sulfur dioxide seems unlikely. Furthermore, the normal coordinate treatment of the fundamental oscillations, though it gives a solution for the triangle with small apex angle which approximately fits the observed frequencies, requires that the binding between the two symmetrically placed atoms be very much smaller than between the other pairs. It is very improbable that the pair of atoms of closest approach should be so weakly bound.

It seems possible that Gerhard has chosen the lowest fundamental frequency wrongly, since Wulf[3] has shown it to be approximately 400 cm^{-1}; and it is rather unlikely that the error in his estimate is as large as would be required by Gerhard's analysis. If this is the case, his explanation for the band at 4.7μ is not valid, since the only band to be expected in this region should be $2\nu_3$, which should have extremely small intensity.

Some years ago G. N. Lewis suggested a probable similarity in the structures of ozone and sulfur dioxide, which is supported by a comparison of their spectra. Mecke[4] has given an analysis of the sulfur dioxide bands compatible with an apex angle of the triangle about 120°, and it appears to the writers that the ozone spectrum may be given a similar analysis which is rather more plausible than that of Gerhard. A comparison of the spectra is made in Table I, where the predicted type of band, whether doublet

TABLE I.

Designation	ν_2	$\nu_1-\nu_2$	$2\nu_2$	ν_1	ν_3	$\nu_2+\nu_3$	$2\nu_1$	$\nu_1+\nu_3$
Predicted type	*D*	*D*	*D*	*D*	*Z*	*Z*	*D*	*Z*
O_3	~440(?)	—	(879?)	1050(*D*)	1355(*Z*)	—	~2110(?)	—
SO_2	~525(?)	606(*D*?)	(962?)	1152(*D*)	1361(*Z*)	1871(?)	2305(*D*)	2502(?)

(*D*) or with central branch (*Z*), is indicated above, and the observed type after the wave number of the band center.

It is rather difficult to decide in some cases, when insufficient resolution has been employed, whether a given band is of the one type or the other, especially if the central branch is weak. This is the case with sulfur dioxide, particularly in the band at 2502 cm^{-1}, which from the measurements of Meyer, Bronk and Levin[5] appears to be a doublet, but which almost any analysis requires to have a central branch.

The best way to clear up any remaining uncertainties seems to be to study the fundamental band of lowest frequency, which so far has not been done for either of the gases.

RICHARD M. BADGER
LYMAN G. BONNER
California Institute of Technology,
January 26, 1933.

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